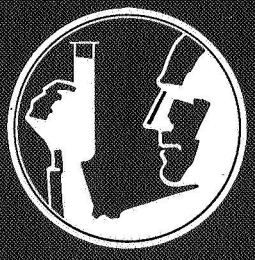
THE DEVELOPMENT OF A LIGHTWEIGHT COATED LIFERAFT FABRIC WITH IMPROVED ABRASION RESISTANCE

Final Report to

MANNED SPACECRAFT CENTER
National Aeronautics and Space Administration

Project 1694, Report 39
Contract NAS9-4189



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NASA CR 99538

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Southern Research Institute
Birmingham, Alabama
October 15, 1968
9308-1694-XXXIX

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ABSTRACT

A process was developed for the continuous production of polypropylene filaments with tenacities of 13 grams per denier. Fifty pounds of multifilament high-tenacity yarns were made by this process for weaving into fabric for the preparation of a coated liferaft fabric. The process for producing high-tenacity filaments consists of melt spinning the filaments under conditions that permit only slight crystallization to occur in the filaments and then producing a high degree of orientation of the polymer chains in the filaments in a two-stage continuous drawing operation.

Twisting and weaving were done by a subcontractor who reported difficulties in these operations, primarily because of filament breakage. The high-tenacity filaments are inherently more brittle than filaments of normal tenacity. The twisting difficulties were overcome by the use of a lubricant and twisting conditions that we recommended. The weaving difficulties were reported to vary from only moderate to severe at different times and were not completely solved at the end of the program. Over 110 yards of fabric of 2/2 twill and basket weave constructions had been woven when resistance to burning became of paramount importance to NASA. Further work on the polypropylene fabric was halted because neither the polypropylene fabric nor the coating that was to be applied to make a liferaft fabric was fireproof.

Polyurethane coatings were specified for use on the liferaft fabrics. Investigation of this class of coating materials led to the conclusion that soluble gums would be the most desirable for use on the liferaft fabric.

Attempts to produce either dyeable or dope-dyed, high-tenacity polypropylene filaments through use of additives were unsuccessful, presumably because the additives induced crystallization before the filaments could be oriented.

THE DEVELOPMENT OF A LIGHTWEIGHT COATED LIFERAFT FABRIC WITH IMPROVED ABRASION RESISTANCE

I. INTRODUCTION

NASA became interested in high-tenacity polypropylene as a result of reports of work carried out at Southern Research Institute for the Office of Naval Research under Contract Nonr-3772(00)(X). In that work polypropylene monofilaments having tenacities of about 13 g/denier were made by drawing short sections of fiber under static loads in an oven. Since the major objective of that program was to define the characteristics of molecular structure necessary to obtain high-tenacity polypropylene fibers, little effort was devoted to producing such fibers on a continuous basis.

Fabrics of high-tenacity polypropylene yarn were of interest to NASA because they offered a possible way to reduce the weight of the liferafts carried aboard space vehicles. Nylon fabrics coated with neoprene are commonly used for liferafts and such coated fabrics conforming to specification MIL-C-19377A have been used by NASA. High-tenacity textile-grade nylon 66 yarn has a tenacity of approximately 9 g/denier and a density of 1.14. High-tenacity polypropylene yarn can be made with a tenacity of about 13 g/denier and the density is only 0.92. Thus, theoretically, it should be possible to produce a polypropylene fabric equal in strength to nylon fabric but weighing less than 60% as much.

At the time this program was undertaken for NASA, it had not been established that high-tenacity polypropylene yarns could be made on a continuous basis, and, therefore, the first part of this program was concerned with investigation of the feasibility of producing such yarns continuously in sufficient quantity for the preparation of samples of fabric for evaluation. It was desired to keep the process-development effort to a minimum.

When it was demonstrated that multifilament polypropylene yarn with a tenacity of about 13 g/denier could be produced continuously and sample fabrics had been woven, the objectives of the program were expanded to include the production of sufficient yarn to permit weaving of fabrics for the production of liferafts.

Attempts were made to produce dyeable or dope-dyed, high-tenacity propylene filaments, but the presence of any additives prevented the development of high tenacity in the filaments.

Also, since some elastomeric polyurethanes were reportedly more resistant to abrasion than the neoprene being used for coating of nylon fabric, there was the possibility that further reduction in weight could be obtained by the use of a polyurethane coating on the polypropylene fabric. Therefore, polyurethane coatings were investigated, as coatings for high-tenacity polypropylene fabrics.

A limited investigation was made of adhesives for sealing and bonding joints in the construction of liferafts.

Near the end of this program, NASA decided that a polypropylene fabric coated with a polyurethane would not be satisfactory for the liferafts because it was flammable, and attention was turned to weaving high-tenacity fabrics with a construction suitable for parachutes. NASA is now considering other possible applications for high-tenacity polypropylene.

II. SUMMARY

The major results from this program were as follows:

A. Preparation of Multifilament Yarns

A process was developed for the continuous production of multifilament yarns of high-tenacity multifilament polypropylene yarns. The process consisted of melt spinning filaments, quenching them in cold water (0 to 3°C) immediately after extrusion to prevent development of crystallinity, and then orienting the spun filaments in a two-stage drawing operation in which they were first cold-drawn and then drawn at 135°C to attain a molecular orientation of about 85%. The yarns listed in Table I, all of which had a nominal tenacity of 13 g/denier, were prepared by this general process and supplied to Prodesco, Incorporated, for weaving into fabric.

Table I. Yarn Shipments to Prodesco

Sample	Yarn denier	No. of filaments	Packages in shipment	Net weight, lb	Date shipped
4295-31A	40	6	7	~1	May 19, 1966
-31B	53	8	7	~1	May 19, 1966
-80-23	55	5	7	1.1	Sept. 6, 1966
-27	40	4	7	0.7	Sept. 16, 1966
4319- 5A	55-60	8-9	74	13.3	Feb. 7, 1967
- 5B	55-60	8	20	2.1	April 7, 1967
- 9A	38-44	6-8	60	3.6	Feb. 10, 1967
- 9B	38-44	6	23	1.3	Feb. 28, 1967
- 9C	38-44	6	54	3.1	Feb. 28, 1967
-13	48-55	8	52	3.2	Feb. 10, 1967
-33	53-66	8	120	9.5	Sept. 14, 1967
-39	40-52	6-7	78	4.4	Sept. 15, 1967
-42	40-52	6-7	80	6.2	Sept. 27, 1967

B. Dyeing of High-Tenacity Polypropylene Yarn

Efforts to prepare high-tenacity polypropylene yarn containing nickel and aluminum salts to serve as dye acceptors to permit vat dyeing fabrics were unsuccessful as were efforts to prepare dope-dyed yarns by incorporating a pigment in the polymer. When these additives were present in the polymer, it was not

possible to attain the very high molecular orientation required in high-tenacity polypropylene filaments. The cause of the difficulties was not definitely established but it seems likely that these additives served as nucleating agents and induced premature crystallization.

C. Weaving of Fabrics of High-Tenacity Polypropylene Yarn

Fabrics of high-tenacity polypropylene yarn were woven by Prodesco, Incorporated. The operations were not witnessed by representatives of the Institute, but discussions with various representatives of Prodesco indicated that difficulties were encountered. It is impossible to identify the exact nature of the trouble without having witnessed the weaving operation, but the most probable cause appears to be the inherent brittleness of the high-tenacity polypropylene filaments. Breakage of filaments in the warp yarns occurred with sufficient frequency to require constant operator attention during weaving. Prodesco did not apply a warp size to the yarn and this certainly contributed to the difficulties. Prodesco found that they could not get adequate adhesion of the size without first treating the yarn with a primer (see Section D below) and felt that it was impractical to use the primer treatment.

Despite the difficulties encountered, several small samples of fabric and one lot of 95 sq yd of 48-inch fabric was woven.

Two lots of high-tenacity yarn were supplied to Prodesco, each sufficient for the preparation of approximately 100 sq yd of 48-inch fabric. The first of these lots (consisting of Samples 4319-5A, -5B, -9A, -9B, -9C, and -13) was converted into satisfactory fabric with some difficulties as discussed above. The second lot (consisting of Samples 4319-33, -39, and -42) was expected to give far less trouble in weaving than the first lot. This yarn was carefully inspected before it was shipped to Prodesco and was found to be superior in filament uniformity to the previous lot. Conditions for twisting this yarn in a downtwister were established at the Institute, and Prodesco reported that they had no difficulty in twisting the yarn and anticipated that this yarn would handle satisfactorily in the loom. When Prodesco beamed the warp yarn, they found that there were more slubs in the yarn than they had anticipated but these were carefully removed and there was every expectation that the weaving would proceed satisfactorily. This expectation appeared to be confirmed by an initial trial in which a yard-long section of 48-inch fabric of 2/2 twill construction was produced. At this point, weaving was stopped since NASA decided to have the remainder of the yarn woven into a rip-stop construction. Due

to several circumstances, the resumption of weaving was delayed almost 4 months, during which time the warp yarn remained on the beam. When weaving was resumed, great difficulties in weaving were reported, again because of breakage of filaments in the warp yarns, and NASA authorized Prodesco to stop the weaving. Prodesco reported that the weaving had improved as they got farther into the beamed yarn, but there was no assurance that the operation would ever become entirely satisfactory. It appears that the long storage of the warp yarn on the beam caused deterioration of the warp yarn, but this has not been established.

The fabrics woven by Prodesco in this program are listed in Table II.

Table II. Description of Fabrics of High-Tenacity Polypropylene Prepared by Prodesco

Sample 4319-49-	Construction	Quantity, sq yd	Fabric strength lb/in. Warp	Fill
1A	1.6 oz 2/2 twill, 160 ends, 100 picks	2	110	100
2	1.6 oz 2/2 twill, 160 ends, 100 picks	3	120	100
3	1.6 oz, basket weave, 156 ends, 100 picks	3	85	105
4	1.6 oz 2/2 twill, 160 ends, 100 picks	95	120	115
5	1.6 oz 2/2 twill, 156 ends, 101 picks	1		
6	rip-stop, 160 ends, 92 picks	-a	-	-
7	rip-stop, 160 ends, 83 picks	-a	-	-
8	rip stop, 160 ends, 85 picks	-a	-	-
9	rip-stop, 160 ends, 84 picks	7.5	-	-

a. Quantity not known.

D. Coatings for High-Tenacity Polypropylene Fabrics

NASA specified a polyurethane coating for the high-tenacity polypropylene fabric because of the high abrasion resistance that is characteristic of polyurethanes. A wide variety of polyurethane coating materials are available, and it was necessary to restrict the investigation to a few examples of the three basic types. These were: (1) non-curing gum stocks, which are applied either from solution or by calendering; (2) sulphur-vulcanizable gum stocks, which also can be applied either from solution or by calendering and finally cured at elevated temperatures; and (3) two-component types, which undergo chemical curing. Preliminary experiments with coating materials of each type showed that none of them would adhere satisfactorily to untreated polypropylene fabric.

Inquiries to several industrial laboratories and a survey of the literature uncovered a large number of suggested procedures for the treatment of polypropylene to improve the adhesion of various coatings. Most of the suggested treatments were ruled out as impractical, since it was obvious that their use would result in an extensive damage to the fabric. Of the several treatments that were tried, the one that proved most effective involved simply saturating the scoured fabric with a 5% solution of di-n-butylmonophosphoric acid in methyl ethyl ketone and drying the fabric at a temperature of 80°C. This treatment did not cause any decrease in the strength of the fabric and a variety of polyurethane coating materials adhered adequately to fabrics treated in this way. A brief discussion of the investigation of several types of polyurethane coatings follows:

Estane polyurethanes supplied by B. F. Goodrich Chemical Company were selected as representatives of the non-curing gum type of polyurethane. Estane 5710 was found to be reasonably satisfactory for the polypropylene fabric although its resistance to blocking was not adequate and NASA preferred a more abrasion-resistant coating. Coatings of Estane 5710 could be applied with commercial coating equipment.

Elastothane supplied by Thiokol Chemical Corporation was selected as representative of the sulfur-vulcanizable gum type of polyurethane. The properties of coatings of this polyurethane were attractive, but the curing time and temperature required (at least 3 hours at 125°C) were both greater than desired.

Special attention was given to two-component type polyurethanes, since it was known that these could yield films with exceptionally good abrasion resistance. Of the several polyurethanes of this type examined, those most resistant to abrasion were based on Adiprene L-100, an isocyanate-terminated prepolymer supplied by E. I. du Pont de Nemours and Company, that is cured with a diamine. Although coatings of this type have the high abrasion resistance desired, they are relatively stiff and would be very difficult to apply with plant-scale equipment.

A moisture-curing polyurethane supplied by Nopco Chemical Company was found to be satisfactory for use in the vehicle for a thin color coat for application to the back of the fabric.

In general, coatings of the two-component, chemical-curing type of polyurethane were the most satisfactory from the standpoint of adhesion and physical properties. Since this type of coating could be designed with almost any degree of flexibility desired, it would have been possible to realize with this type of polyurethane a reasonable compromise of flexibility, abrasion resistance, and resistance to blocking. It is likely that applications of this type of coating in plant-scale equipment would have presented some problems.

E. Adhesives

At the outset of the program, it was thought that the development of a polyurethane adhesive for assembling liferafts would not present any particular problems, but following discussions with representatives of NASA, it became apparent that it would be necessary to have an adhesive with an 8-hour pot life — a requirement that had not been anticipated. Two solutions to this problem were found.

An adhesive based on DDI — an isocyanate derived from a dimer acid supplied by General Mills, Incorporated — was particularly effective. This adhesive was prepared by mixing the DDI with Modified Amine A-100 (General Mills). This curing agent is an amine complex that is decomposed by water to release the amine and the amine then combines with the DDI. If reasonable precautions are taken to protect this mixture from moisture, the mixture with DDI will have a pot life of at least 8 hours. Once the film of adhesive is applied, moisture in the atmosphere initiates the release of the amine and curing of the adhesive.

A second type of adhesive, and a more conventional one, is based on Estane polyurethane gum (B. F. Goodrich). The adhesive compound is prepared by adding 15 parts of methylene-bis(4-phenylisocyanate) to 100 parts of Estane polyurethane gum dissolved in methyl ethyl ketone. This adhesive can be brushed onto the surfaces to be bonded and, as soon as most of the solvent has evaporated, the pieces can be joined. This adhesive cures by reaction of the diisocyanate with active hydrogens in the polymer. This mixture is sufficiently stable to allow use over a period of at least 8 hours.

F. Materials, Equipment, and Procedures

Descriptions of the materials, equipment, and procedures used in this program are given in the appendix of this report.

III. PRODUCTION AND PROPERTIES OF YARNS

The development of the process for producing high-tenacity yarns continued over most of the period of this program with improvements and refinements being made as the program progressed. In the following discussion, information gained throughout the course of the program is brought together to indicate the nature of the problems encountered and the solutions that were developed.

The study of high-tenacity polypropylene fibers carried out at the Institute for the Office of Naval Research (Contract NONR-3772(00)(X)) served to define the characteristics of molecular structure and some of the conditions of processing necessary to obtain high-tenacity polypropylene fibers. That study indicated that the following were necessary, or at least highly desirable:

- The isotacticity of the polymer used for spinning should be 94% or greater, but a completely isotactic material appeared to be undesirable.
- The polymer should have a molecular weight of at least 400,000.
- The fiber should be quenched rapidly to a low temperature immediately after extrusion.
- The fiber should be taken up at a slow enough rate during spinning to minimize molecular orientation (preferably only about 0.1).
- Subsequently, the fiber should be highly drawn to produce a molecular orientation value of over 0.80.
- The fiber should not be highly crystalline (less than 50%).

These findings served as guides in the development of a continuous process for making high-tenacity polypropylene yarn in the present program.

A. Preliminary Experiments on the Production of High-Tenacity Yarns

1. Equipment

The equipment used in preliminary experiments was similar but not identical to that described in Section A.1. of the appendix. The major difference was in the spinning head. The head used in the early work was purchased from Killion Extruders,

Inc. and temperature control in this head was not as good as that obtained in the head used during the later production of yarn. Also, the temperature control in the extruder proper was improved for later work. The spinneret used in the early work had eight orifices, 12 mils in diameter and with a 4:1 length-to-diameter ratio.

2. Melt spinning

Initially, we attempted to melt spin Profax 6723 (the polymer used for most of the program) at a temperature of 260°C but found that even at a polymer flow rate of 2.8 g/min (the lowest we could obtain with the equipment available) melt fracture occurred. To eliminate melt fracture, it was necessary to raise the temperature in both the spinning head and the extruder to such an extent that considerable thermal depolymerization of the polymer occurred. Since high molecular weight was desirable for producing high tenacity, there was some concern over the effect of this depolymerization. Several yarns were melt spun under conditions that appeared feasible for continuous operation in the equipment, and filaments from these yarns were oriented under static loads in an oven in the same manner as in the program carried out for the Office of Naval Research. Filaments with tenacities above 12 g/denier were obtained, demonstrating that the thermal depolymerization was not excessive. It appeared at this stage of the program that the best operating conditions for melt spinning were as follows: Temperatures of 275°C in the extruder feed zone, 300°C in the metering zone, and 300°C in the spinning head; a polymer extrusion rate of 5 g/min; and a yarn take-up rate of 90 ft/min. Under these conditions, we made filaments in which the molecular orientation value was about 0.15.

3. Orientation

Investigation of the continuous orientation of yarns prepared under the conditions described above was then undertaken. Conventional methods such as stretching between heated godets, stretching over a heated shoe, and stretching with a combination of heated godets and a heated shoe were tried. Temperatures and yarn feed rates were varied, but no conditions were found that produced yarns having tenacities above 10 g/denier. It appeared that a fairly long time under tension was necessary to obtain the high tenacities required. Accordingly, we tried stretching the yarns in a 10-foot-long oven and found that we could make yarns with tenacities of about 13 g/denier, but only with a maximum output rate of about 30 ft/minute. A study of the effect of oven temperature showed that it was desirable to have the temperature in the range of 120 to 140°C. If the

temperature were much lower than this, the maximum tenacity attainable was less, and, if the temperature was higher, there was a tendency for the fibers to fuse, but temperature in the range of 120 to 150°C was not critical. Attempts were made to increase the output rate by passing the yarn through the oven once while stretching it to produce a tenacity of about 10 g/denier and a second time to further increase the orientation and obtain higher tenacity. Although considerable stretching was accomplished during the second pass, there was no significant increase in the tenacity of the yarn.

A two-stage stretching operation was then tried in equipment very similar to that shown in Figure 11 in the appendix. The yarn was stretched at room temperature between the feed godet and a second godet (heated to the same temperature as the oven) and then stretched further in the oven. Using this procedure, we were able to produce continuously yarns having the desired tenacity of 13 g/denier at rates of about 150 ft/min. This was a considerable improvement over the rate obtained by single-stage stretching.

Numerous experiments were made in an effort to establish the effects of varying the cold-draw ratio, the oven temperature, and the throughput rate on the properties of the oriented yarns, but the reproducibility of the experiments was so poor that no definite conclusions could be reached. The search for the causes of the poor reproducibility was rewarding because it disclosed the importance of some variables that had not previously been thought significant. The major factors that were contributing to the poor reproducibility in these experiments are discussed below.

The polypropylene filaments having low molecular orientation were easily stretched even at very low stress levels, and, as a consequence, some uncontrolled cold drawing of the yarns occurred in equipment used to feed the yarns to the orienting equipment. As will be discussed in more detail later, the optimum draw ratio for making high-tenacity filaments depends to some extent upon the molecular orientation in the filaments being fed to the drawing equipment, and, therefore, this uncontrolled drawing in the feed equipment caused variations in the tenacity of the oriented yarns.

The amount of water retained on the yarns and the time between spinning and drawing were also found to affect the behavior of the yarn during orientation. Yarns that could be oriented to the desired tenacity within a few hours after they were spun could not be oriented satisfactorily under the same conditions after they had aged several days.

Another factor causing variations in the properties of the oriented yarns was that the molecular weight of the extruded polymer was found to be varying considerably because of slight fluctuations in the temperature in the feed zone of the extruder. The temperature in the feed zone of the extruder had far more effect on molecular weight of the extruded polymer than was anticipated. We also found some bag-to-bag variation in the melt viscosity of Profax 6723.

The observations made during these preliminary experiments provided considerable insight into the requirements of a process for making high-tenacity polypropylene yarn on a continuous basis. It is well known that very slight changes in orientation result in large changes in tenacity at these high levels of tenacity, and minor changes in processing conditions can have a large effect on the orientation of fibers.

4. Conclusions from preliminary experiments

We postulated that the two-stage stretching was effective for producing high-tenacity fibers because it allowed the development of considerable orientation at a temperature at which the rate of crystallization was low, and then produced the remainder of the orientation before crystallinity was fully developed. This postulate has not been experimentally verified by studying the parameters of molecular structure at various stages of processing, but many observations made in the preliminary experiments and later in the program provided substantiation.

At this stage of the program it had been demonstrated that multifilament yarns having tenacities of about 13 g/denier could be made continuously. However, the filaments in the yarns made at this stage were much larger (about 20 denier) than desired (about 5 denier), and ways to reduce the filament size were sought next.

B. Efforts to Reduce Filament Size

The principal factors that determine the size of filaments in melt spinning are: (1) the diameter of the orifice of the spinneret, (2) the draw-down between the spinneret and the take-up, and (3) the draw ratio in orienting the yarn. The total draw ratio is the product of the denier reduction ratio between the spinneret and the take-up during spinning and the denier reduction ratio during orientation. Figure 1 shows the calculated filament denier as a function of total draw ratio for orifices of different diameters.

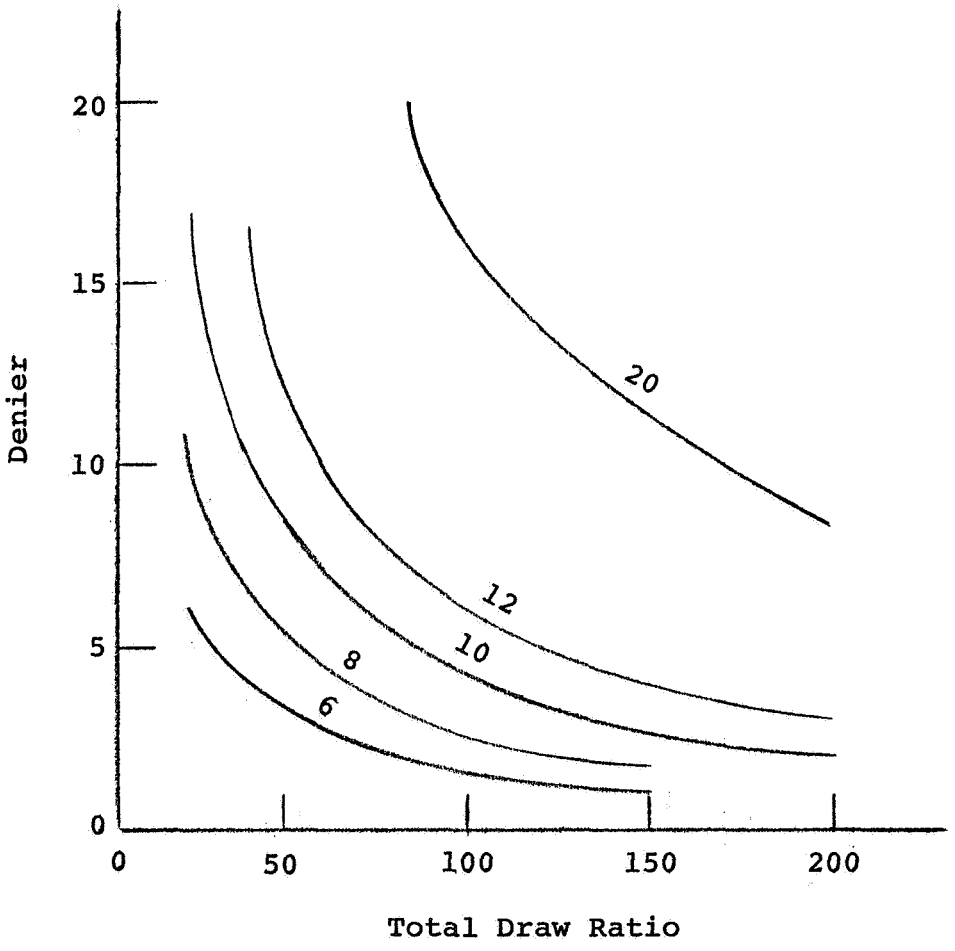

Figure 1. Denier vs. Total Draw Ratio for Fibers Extruded from Orifices with Different Diameters

In early stages of the program it was assumed, on the basis of previous work, that low molecular orientation in the melt-spun filaments was very desirable and probably essential. Accordingly, efforts in this phase of the program were concentrated on attempts to reduce the size of the filaments while maintaining low orientation.

It was quite apparent that it was desirable to have the viscosity of the extruded polymer as low as possible to favor a reduction in filament size by permitting the use of small orifices and by allowing greater draw-down during spinning without increasing orientation. The viscosity of the polymer flowing through the orifices of the spinneret is determined by the molecular weight of the polymer and by the temperature of the polymer. However, the extent to which the molecular weight of the polymer could be reduced was limited, because it is not possible to orient the yarns enough to attain a tenacity of 13 g/denier if the Extrusion Index of the extruded polymer is less than about 2.0. There was also a limit on the maximum temperature to which the polymer could be heated without causing too great a lowering of molecular weight.

Considerable effort was devoted to attempts to melt spin satisfactory yarns through a spinneret with 9-mil orifices, but with the spinning equipment available it was not possible to obtain low enough shear rates through the orifice to make uniform filaments (See Section III-D for a discussion of factors influencing filament uniformity). A polymer extrusion rate of 2.8 g/min was the minimum attainable. An attempt to reduce the shear-rate by installing by-pass orifices resulted in nonuniform distribution of polymer to the spinning orifices.

The effect of distance between the face of the spinneret and the surface of the water in the quench bath on orientation in the spun filaments was then investigated in the hope that by varying this distance it would be possible to obtain higher draw-down ratios without increasing orientation. Yarns were melt spun with the distance between spinneret face and quench-bath surface ranging from 1 to 18 inches, but no significant effect on the orientation in the filaments could be demonstrated. The best distance from the standpoint of operability was 4 to 5 inches. With shorter distances, cooling of the face of the spinneret and thermal air currents caused operational problems, and, with greater distances, it became more difficult to keep the filaments separated.

Another approach to increasing the draw-down ratio without increasing orientation involved the use of a small heated spinway between the spinneret and the quench bath. The rationale for this approach was that keeping the filaments heated for a longer time might allow the polymer molecules to relax. The operational problems involved in spinning through a heated spinway proved to be difficult, and we did not judge it desirable to expend the amount of effort on this approach that would have been necessary to allow us to operate with a spinway as long or as hot as desired. We did spin through a heated spinway 3 inches in length, but, as the data of Table III show, the molecular orientations in the filaments spun in this way were higher than in filaments spun without the spinway.

These results led us to the investigation described in the following section.

Table III. Effect of Spinning through a Heated Spinway on Molecular Orientation[a]

	Molecular orientation		
Spin draw	No tube	Tube at 245°C	Tube at 300°C
6X	18	20	-
8X	22	39	-
10X	31	46	73

a. Filaments were spun through an 8-hole spinneret with 12.2-mil orifices at a rate of 5 g/min.

C. Investigation of the Effect of Orientation in the Melt-Spun Yarn

The experiments described in Section III.B. showed that it would not be possible to make filaments as small as desired by melt spinning small filaments with low molecular orientation, and also that there were some mechanical problems in handling yarns of filaments with low orientation. These results prompted an investigation of the effect of orientation in the melt-spun filaments on the tenacity of fully oriented yarn.

A typical relationship between the draw-down ratio and the molecular orientation in filaments of the spun yarn is illustrated by the data in Figure 2. These data were obtained in an experiment in which all other processing conditions were held constant.

Figure 3 shows a plot of molecular orientation vs draw-down ratio during spinning for filament yarns made with widely varying processing conditions. The scatter of the data indicates that some factors other than draw-down ratio affect the orientation, but it is apparent that the draw-down ratio is the dominant variable. Other factors that we would expect to influence the orientation are the molecular weight of the extruded polymer, the shear-rate through the orifice, the length-to-diameter ratio of orifice, and the temperature of extrusion. It was not worthwhile to explore all of these variables, since their effects appeared to be minor.

Several yarns were spun with different amounts of spin drawing to produce different degrees of molecular orientation in the filaments. Then, they were oriented in equipment similar to that shown in Figure 11 in the appendix. The oven and the intermediate and take-up godets were operated at 135°C. In the first experiments with these yarns, the draw ratio between the feed godet and the intermediate godet was 1.5X and the total draw ratio was adjusted to the maximum that did not induce microfractures in the filaments.

The results of these first experiments were surprising since they indicated that the tenacities of the final oriented yarns increased as the orientation of the filaments after spin drawing increased. The only yarn with 13 g/denier tenacity produced in these experiments was made from yarn with filaments spin drawn to have a molecular orientation of about 0.5, which was much higher than the value thought previously to be the maximum permissible. To produce spun filaments having this level of orientation, the draw-down during spinning had to be above 20:1, and at this high draw-down the uniformity of the filaments was poor. So even though high orientation in the melt-spun filaments appeared to be desirable from the standpoint of strength the poor uniformity of the filaments made them unacceptable.

A study was then made of the effect of the extent of cold drawing on the tenacity of oriented yarns made from yarns with filaments that had been oriented to different degrees. Although this study did not show a definite correlation between the optimum cold-draw ratio and the orientation in the filaments of the yarn, it did show that yarns of satisfactory tenacity could be made from any of the yarns provided the extent of cold draw was adjusted to compensate for differences in the orientation of the filaments before cold drawing.

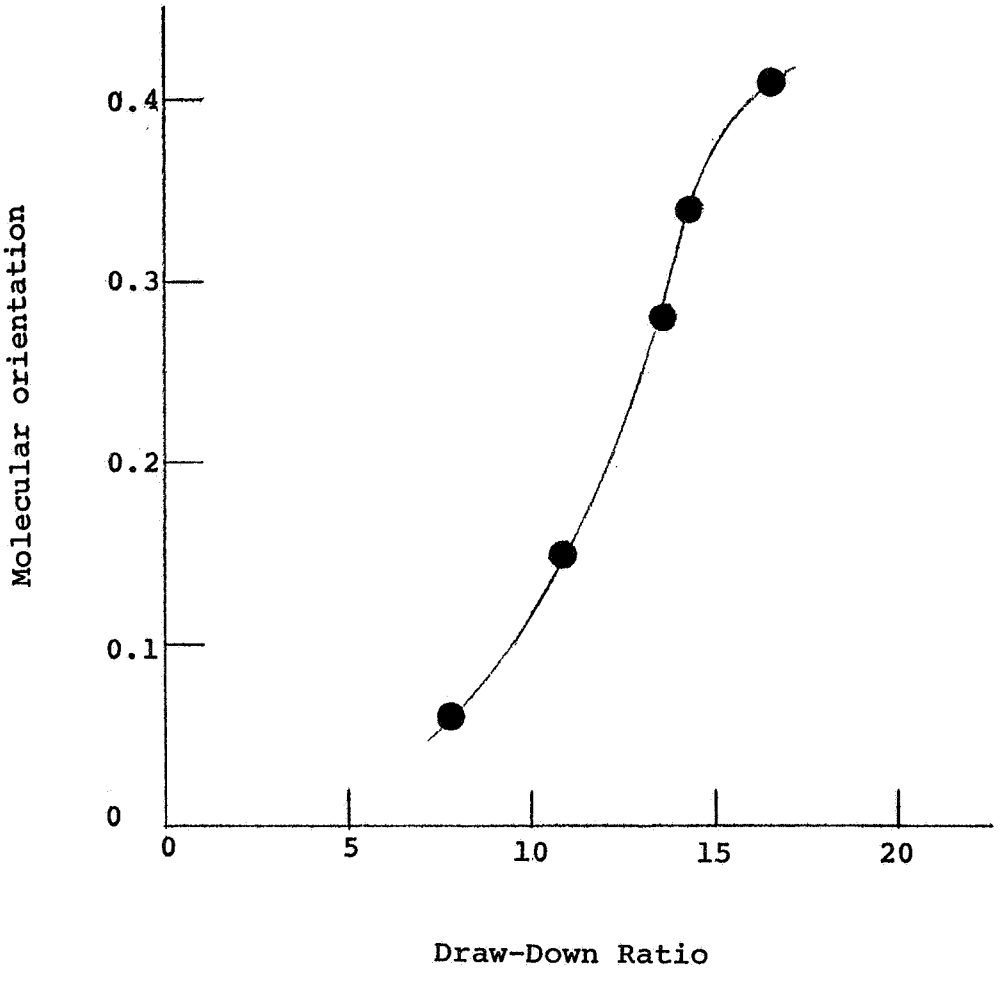

Figure 2. Typical Relationship Between Molecular Orientation in Melt-Spun Filaments and Draw-Down Ratio During Spinning

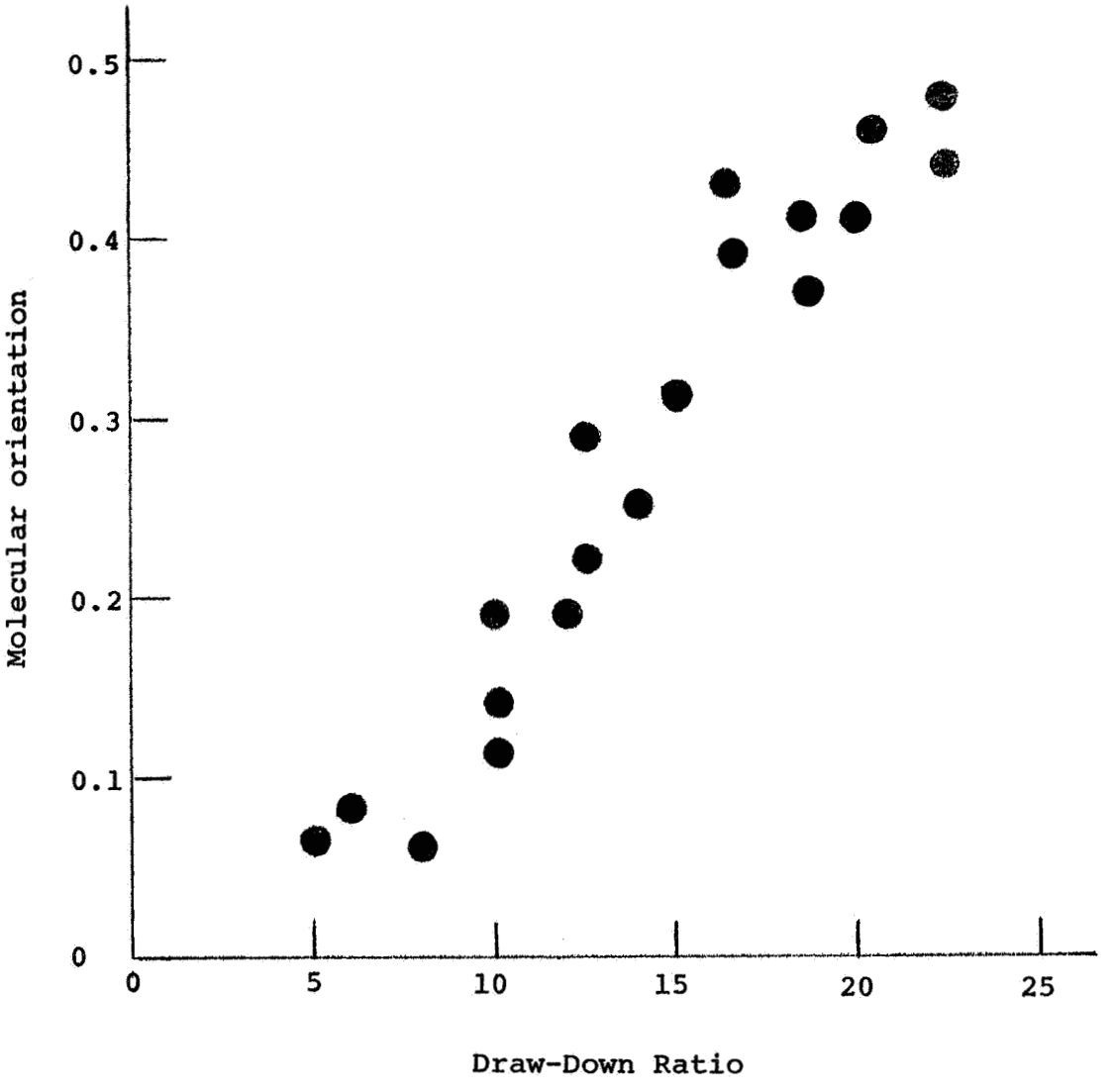

Figure 3. Molecular Orientation vs. Draw-Down Ratio During Spinning for Filaments Spun Under Various Conditions

In the production of high-tenacity yarn, it was found that best results were obtained with yarns oriented during spinning to produce an orientation of about 0.35. Further orientation of yarns having this degree of initial orientation was more trouble-free than with yarns of lower orientation.

At this stage of the program, a satisfactory process had been developed for making high-tenacity polypropylene yarns and it had demonstrated that it was technically feasible to make enough high-tenacity yarn to permit weaving fabric for prototype liferafts. There was evident need for further process development before the process could be considered commercially feasible, but this was not within the scope of the project. With the concurrence of NASA, it was decided to proceed with the preparation of yarn by the process as it stood with the understanding that refinements and improvements would be made as experience was gained.

D. Problems During Production of High-Tenacity Yarns

Although no efforts were expended with the specific objectives of making improvements in the processing procedures, some improvements were made in the course of solving specific problems as they arose during the production of yarns for weaving. Some of the more important of these problems are discussed below and the final procedures adopted for overcoming these problems to a satisfactory degree are summarized in Section III-G.

1. Filament uniformity

Nonuniformity of the filaments in the yarns was a major problem throughout this program, and one that was not completely solved. It is important that all filaments in a yarn be uniform in diameter along their length and that all of the filaments in a yarn be of the same diameter because, during orienting, the filaments are held under a tension of about 5 g/denier at a temperature of 135°C, which means that the filaments are under a stress very close to the breaking point. If there is appreciable nonuniformity, the stress must be held lower than desired for obtaining maximum tenacity or there will be excessive filament breakage. As a further complication, the optimum cold-draw ratio in the orienting process depends upon the extent of molecular orientation at the start of the operation, and the molecular orientation in the filaments is not likely to be uniform, either along the length of the filaments or from filament to filament, if the filaments are not uniform in diameter.

The factors that influence filament uniformity are fairly well-established. When molten polypropylene emerges from the orifice of a spinneret it swells as depicted in Figure 4. This is called the Barus effect and results from the elasticity of the molten polymer. The Barus effect is common with many polymers but is unusually pronounced with polypropylene. Because of the swelling at the orifice, a filament is actually being drawn from a reservoir of polymer and, if anything happens to change the size of the reservoir, the diameter of the filament will change. The greater the swelling at the orifice, the more difficult it is to eliminate fluctuation in the size of the reservoir. Following are the major factors that influence the degree of swelling of polypropylene at an orifice:

- Orifice diameter. At a fixed polymer flow rate, the degree of swelling increases as the orifice diameter decreases, particularly with small orifice diameters.

- Polymer flow rate. The effect of polymer flow rate is best considered in terms of shear rate.* Swelling increases with increasing shear rate, but, at the very low shear rates we used, the effect is not great.

- Polymer viscosity. The viscosity of the polymer flowing through the orifice has a major effect on the degree of swelling, which increases with increasing viscosity. The viscosity of the polymer passing through the orifice is determined by the molecular weight of the polymer (and to a minor extent by molecular weight distribution) and the temperature of the melt.

- Orifice geometry. The greater the length-to-diameter ratio of the spinneret, the less the swelling. The entrance angle of the orifice also has some effect (a 90° angle is less desirable than a 45° angle). This effect is probably very minor in orifices with a high L/D ratio.

Nearly every feature of the melt-spinning process that was desirable from the standpoint of high tenacity and filament-size reduction tended to have an adverse effect on filament uniformity.

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*Shear rate, $sec^{-1} = \frac{4Q}{\pi R^3}$ where

Q = flow rate cm^3 sec^{-1} and R = radius of orifice in cm.

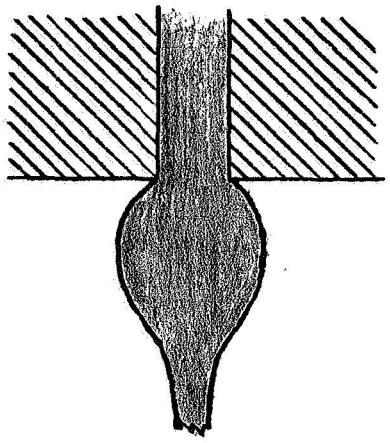

Figure 4. Swelling of Polymer at Orifice of Spinneret (Barus Effect)

It was necessary to quench the extruded filaments in cold water very soon after they emerged from the orifices in order to prevent crystallization of the polypropylene. This mode of quenching created conditions that did not favor good filament uniformity. As the yarn left the quench bath it carried with it water, most of which drained back into the bath. However, the amount of water carried out by the yarn was not constant and this caused fluctuation in the tension on the yarn leaving the bath that was detectable with a tensiometer. Even though much of this fluctuation in tension could be damped by passing the yarn over rolls in the quench bath, some was transmitted to the filaments leaving the spinneret, and even a slight variation in tension was enough to disturb the "reservoir" of molten polymer at the outlet of an orifice. The passage of the yarn through the quench bath created currents in the water, and these also contributed to some extent to variations in the tension on the filaments. The effect of these currents was demonstrated by the improvement in uniformity resulting from placing baffles in the quench bath to minimize the effect of the currents.

The nearness of the surface of the cold quench bath to the face of the hot spinneret (4 to 5 inches), caused some air currents in the zone between the surface of the bath and the spinneret, but there is no evidence to indicate that these air currents had a significant effect on filament uniformity.

Considerable improvement in filament uniformity was made in the course of this program primarily by close attention to small details of the operation, principally involving rigid control of the viscosity of the extruded polymer and minimizing tension fluctuation.

2. Reduction of filament size

Increasing the draw-down during spinning was the most effective means of reducing the size of the oriented filaments. In the water-quench type of operation, for spinning polypropylene, the maximum permissible total draw increased with increasing draw-down during spinning, but not linearly. A typical relationship between draw-down during spinning and maximum permissible total draw is shown in Figure 5. The limit of the total draw was considered to be the maximum permissible without causing fractures.

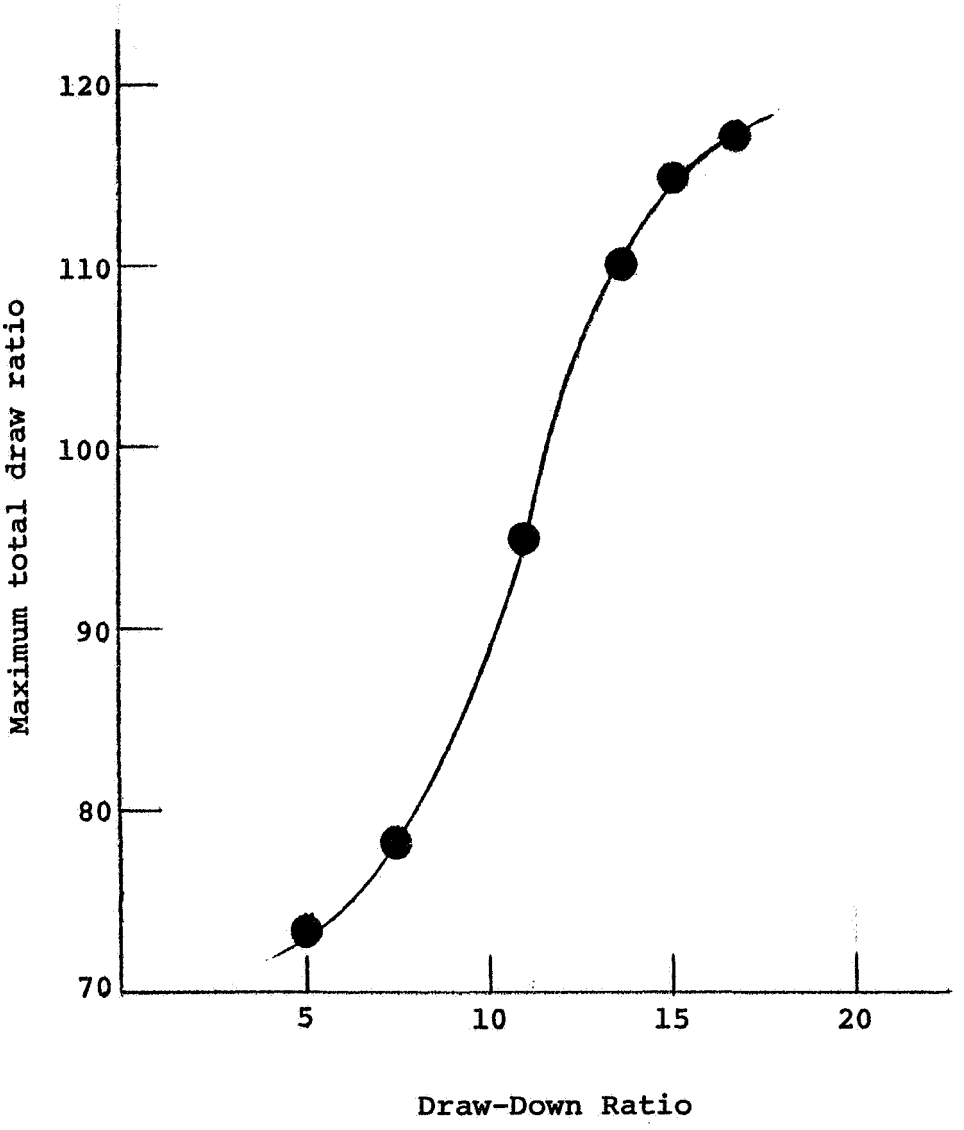

Figure 5. Typical Relationship Between Maximum Total Draw Ratio and Draw-Down Ratio

The relationship of orientation during spinning to total permissible draw-down for polymer having an Extrusion Index of 2.0 spun through a spinneret having 12-mil orifices (12:1 L/D) with varying degrees of draw-down during spinning are given in Figure 6. These yarns were machine drawn to just short of the development of fractures in the filaments. This relationship appears to be the general one for a given polymer and fixed general conditions for orientation. Variations in such factors as orifice size and polymer flow rate do not influence this relationship.

The data in Figures 5 and 6 showed that increased orientation during spinning increased the permissible total draw ratio and was, therefore, desirable from the standpoint of reducing filament size. The amount of draw-down that can be done during spinning is limited since, with all other operating conditions fixed, the filaments will become extremely nonuniform when the draw-down exceeds a critical value. With low draw-down, the uniformity of the filaments decreases only slightly with increasing draw-down until a critical value is reached; further increases in draw-down cause rapid increases in nonuniformity. This is illustrated by the data in Table IV. The diameters of the meltspun filaments were measured with a microscope fitted with a Filar micrometer at 6-inch intervals along 40- to 50-foot sections of a filament, and the ratios of maximum to minimum diameters were calculated. These data show a considerable increase in nonuniformity when the draw-down ratio exceeded 16.6.

Table IV. Example of Effect of Draw-Down in Spinning on Filament Uniformity

Draw-down ratio	Ratio max/min diameter
7.8	1.08
10.9	1.08
13.6	1.09
14.4	1.09
16.6	1.11
18.0	2-3

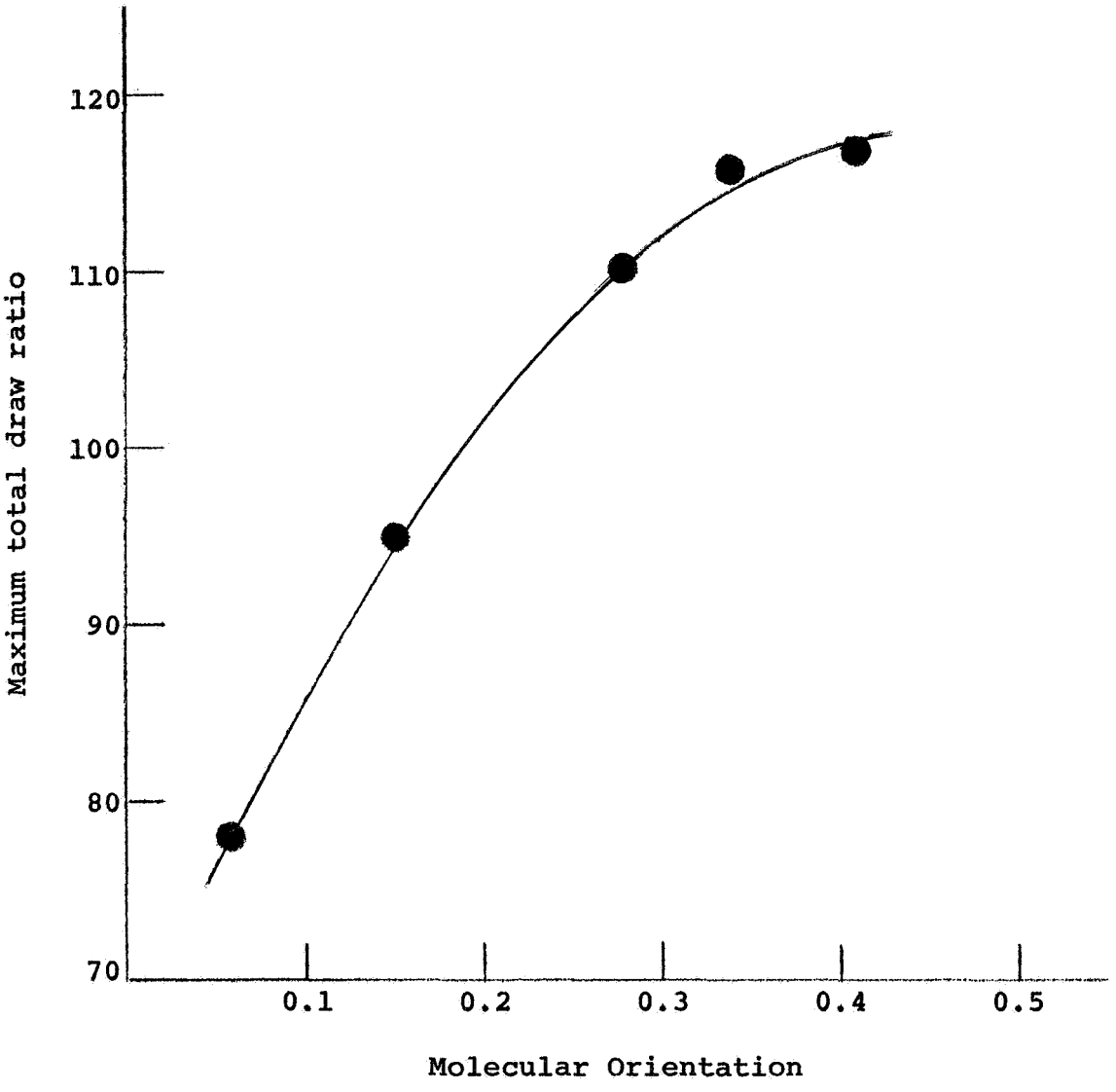

Figure 6. Maximum Total Draw Ratio vs. Molecular Orientation of Undrawn Filaments During Spinning

3. Effects of different orifice dimensions

From examination of the results obtained in spinning with spinnerets with orifices of different diameters, it was concluded that, when melt spinning polypropylene with an Extrusion Index of 2.0 at flow rates in the range of 4-9 g/min (through 16 orifices), the optimum spinneret orifice diameter was about 12 mils. A spinneret with 10-mil orifices showed no advantage either in a reduction in filament size or in filament properties. The possible advantage of the smaller 10-mil orifices was offset by the fact that the maximum draw-down during spinning of filaments spun through them was much less than for filaments spun through 12-mil orifices. The net effect was that the oriented filaments were essentially the same size whether spun with 10-mil or 12-mil orifices. Orifices 16 mils in diameter gave excellent results from an operational standpoint, but the smallest filaments that could be made with orifices of this diameter were about 25% higher in denier than those made with a spinneret having 12-mil orifices.

A high L/D ratio in the orifices was beneficial. With 12-mil orifices, a 12:1 L/D ratio allowed a 15-20% reduction in denier from that obtained with 12-mil orifices with a 4:1 L/D ratio.

4. Orientation

The equipment used for orienting the yarns during the production period is shown in Figure 11 in the appendix. The yarns were stretched between the feed godet and the intermediate godet located just inside the entrance to the oven and then further stretched through the oven at 135°C. Some refinements in the control of the orienting conditions were made during the course of production, but no basic changes were made.

Initially the degree of stretch between the feed godet and the intermediate godet (cold draw ratio) was established by trial and error to the optimum for each lot of yarn processed. Control of the degree of stretch through the oven was tedious and time consuming. The yarns were stretched until the appearance of the yarn (viewed against a black background) changed from clear to opaque white indicating extensive fracture of the filaments. The degree of stretch was then reduced in small increments (about 2% change in speed of final godet) and samples were collected for tenacity determinations. A degree of stretch was then adopted to give maximum tenacity.

As we gained experience with the operation, it became evident that the optimum cold draw ratio was very near to the maximum that could be imparted, and that, if the Extrusion Index of the extruded polymer were held constant, then the optimum cold draw could be predicted from the initial molecular orientation of the filaments being oriented. The relationship developed between optimum cold draw ratio and molecular orientation is shown in Figure 7 for filaments of polymer having an Extrusion Index of 2.0.

Later the following control procedure was adopted. A line-tension-measuring device was installed just ahead of the final godet. The degree of stretch was set to produce extensive fracture and then gradually reduced in small increments with samples being taken for microscopic examination to detect fractured filaments. Figure 8 is a photomicrograph showing two fractured filaments among unfractured filaments. The degree of stretch was then adjusted to be just below that inducing fracture in one or more filaments of the yarn and the line tension was noted. Any deviation in processing would then be indicated by a change in line tension. This technique also provided a simple way to check the uniformity of the filaments in the yarn. The range of draw ratio over which the extent of filament fracture progressed from one fractured filament to fracture of all filaments gave an indication of the uniformity. If the range exceeded 5% of the overall draw ratio in the orienting process, the uniformity was considered questionable.

E. Tenacity of Polypropylene Yarns

The procedure used for measuring the tenacities of the yarns produced in this program (Appendix Section 1.b.) involved determining the denier of a yarn by weighing a measured length and determining the breaking strength of the yarn by totaling the breaking strengths of the filaments in a cross-section. Because of the nonuniformity of the filaments, the precision of measurements of tenacity was not as good as it would have been if the filaments in the yarn had been uniform. Also, there was no assurance that the denier of the small section taken for a tenacity measurement was identical to that of the average for the long section weighed for denier determination.

To provide frequent checks on tenacity, the yarn produced was collected in small packages and tenacity determinations were made on three cross sections. The average of the three determinations was reported as the tenacity of the yarn on the package.

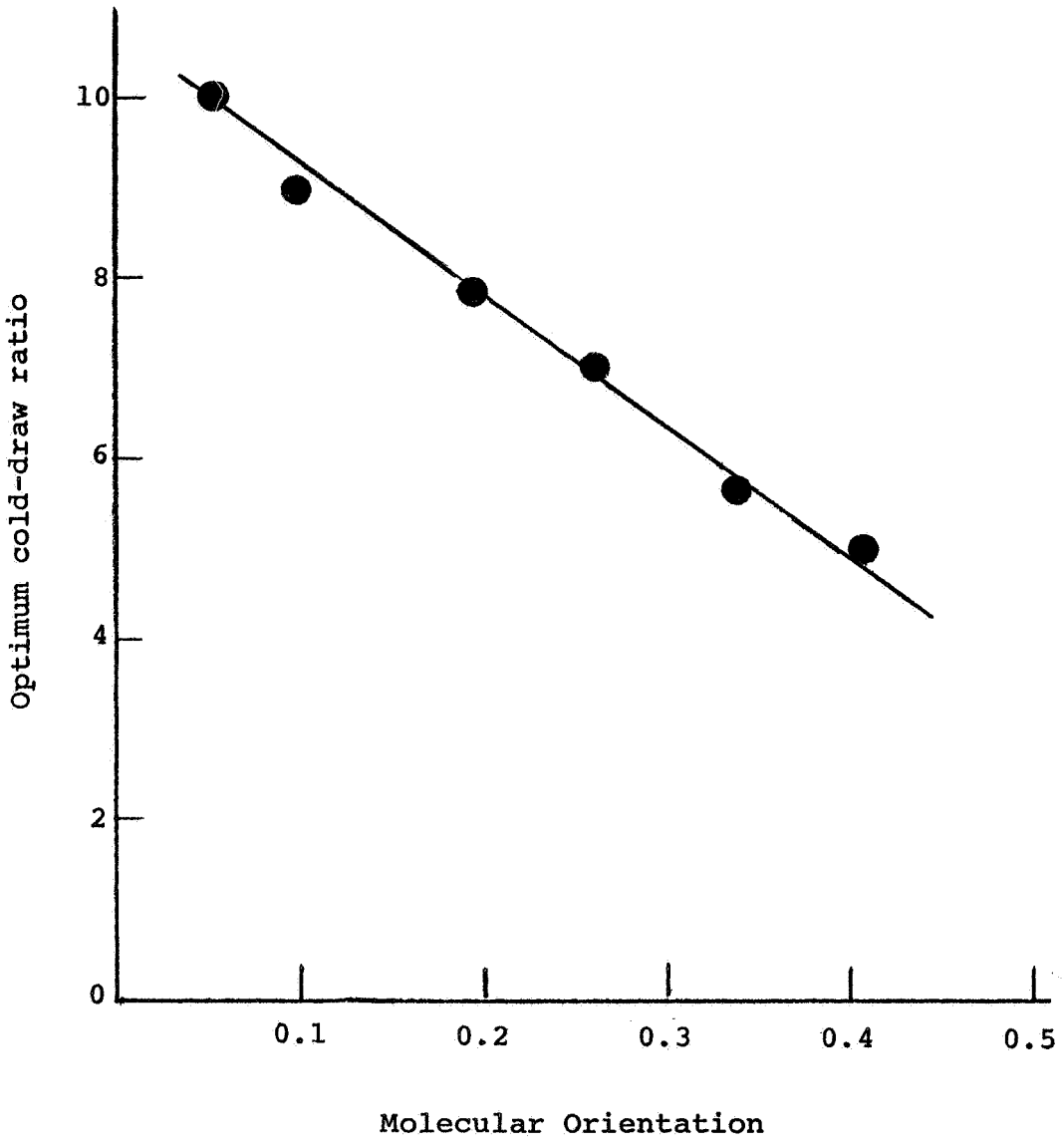

Figure 7. Optimum Cold-Draw Ratio vs. Molecular Orientation of Undrawn Filaments

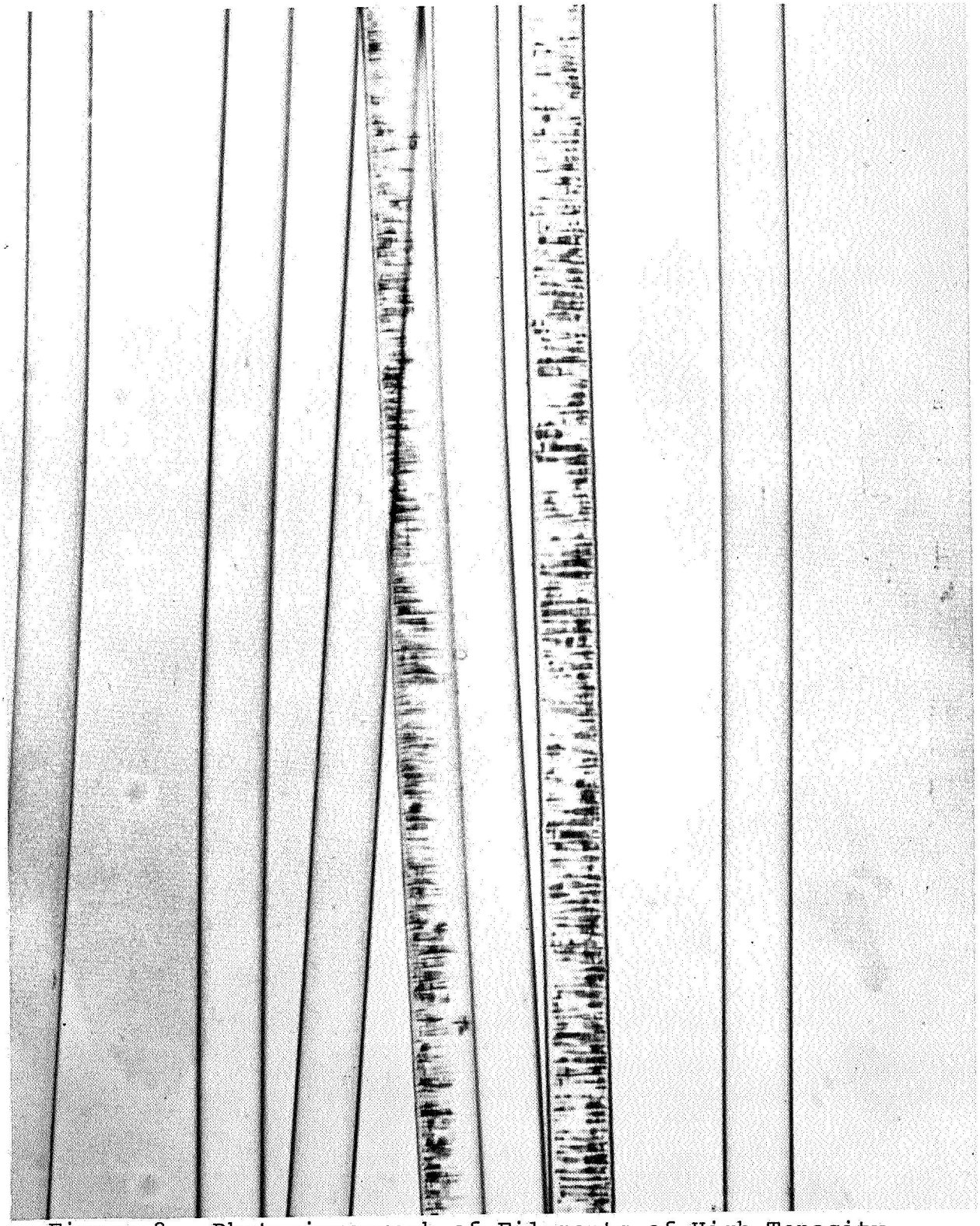

Figure 8. Photomicrograph of Filaments of High-Tenacity Polypropylene Yarn with Two Fractured Filaments

The most accurate way to measure the tenacity of a section of yarn is to determine the denier of each filament in a cross-section of the yarn with a Vibroscope, measure the breaking strengths of the same sections of the filaments, and calculate the tenacity for all of the filaments. This procedure gives consistently higher values for tenacity than the method used for routine determinations discussed above. For example, in one group of 10 yarns the average tenacity for the group determined by the Vibroscope method was 0.5 g/denier higher than the average of the tenacities determined by the routine method, and in another group of 14 yarns the values for tenacity by the Vibroscope method were 0.6 g/denier higher.

To investigate the reproducibility of tenacity measurements, 15 cross sections were taken from a length of 7-filament yarn that was selected to be as uniform as we could expect to produce. The tenacity of each of the specimens of yarn were determined by the routine (weight) method. The standard deviation of the 15 values of tenacity was 1.61 g/denier, thus for averages of three values (the number determined for each package of yarn produced) the standard deviation would be 0.94 g/denier. Based on this result and the above comparison of results obtained by the Vibroscope and the weighing methods of determining tenacity it was concluded that a reasonable lower limit of tenacity for quality control would be 12.0 g/denier, determined as the average for three specimens from a package by the weighing method. This limit undoubtedly resulted in discarding some yarns that would have been found acceptable on further checking but it did assure that very few packages of yarn with tenacities below 12.5 g/denier would be retained.

Non-uniformity along the length of filaments of the high-tenacity polypropylene also caused the gauge length used in making the tenacity determinations to have an effect on the results — the longer the gauge length the lower the indicated tenacity. The yarn denier used in conjunction with the measured breaking load in the calculation of tenacity was an average value but the filaments would tend to break at the points of smallest cross section. The likelihood of including sections of filaments with smaller than average cross sections in the specimens that are broken increases as the gauge length increases. The magnitude of the effect of gauge length on the indicated tenacity can vary considerably depending on the non-uniformity of the filaments, but the tenacities of the yarns produced in this program were generally about 20% lower when determined with a 10-inch gauge length than when determined with a 1-inch gauge length.

The tenacities of twisted yarns of high-tenacity polypropylene are lower than the sums of the tenacities of the individual filaments in the yarns. This effect was studied by selecting 15 to 20 foot lengths of single filaments from yarns and combining 3-inch sections from this to make short lengths of 6- to 8- filament yarns. The breaking strength of the filament was taken as the average of 5 determinations on specimens taken at about equal intervals along the length. The small sections of multifilament yarn were twisted by hand (3 to 4 TPI) and the breaking strengths of the twisted yarns were measured. The breaking strength of the twisted yarn (average of 10 measurements) was 90% of that calculated by multiplying the breaking strength of the filament by the number of filaments in the yarn. In these experiments, variations in filament strength and size within the yarns were minimal, and, therefore, the results were quite consistent. Comparison of the tenacities of machine-twisted yarns (determined by measuring the breaking load of the yarn) and the tenacities determined by the individual-filament method were much less consistent. The results of a large number of such comparisons made over the course of this program indicate that the loss of tenacity to be expected as a result of twisting was 10 to 15%.

F. Final Operating Conditions

Following is a description of the processes for producing high-tenacity polypropylene yarn as developed at the end of the program.

1. Melt spinning

The melt-spinning equipment was set up as described in Section A.1.a. and Figure 9 of the appendix. The spinning head was fitted with a spinneret having 16 orifices each 12 mils in diameter with a 12:1 L/D ratio. The temperatures in the extruder were 268°C in the feed zone, 307°C in the metering zone, and 307-310°C in the spinning head. Profax 6723 was charged to the extruder, the metering-pump speed was adjusted to give an output rate of 7 g/min, and the screw speed of the extruder was adjusted to give a pressure of 1000 psi at the entrance to the spinning head. After the equipment had operated for about 2 hours under these conditions, the Extrusion Index of the extruded polymer was measured. If the Extrusion Index was above 2.0, the temperature in the feed zone of the extruder was raised and if it was below 1.8 the temperature was lowered. Adjustment of the temperature of the feed zone was continued until the Extrusion Index of the extruded polymer remained in the range of 1.8-2.0.

After the melt-extrusion equipment was operating as described above, yarn collection was started with the twin godets rotating at a speed of about 240 peripheral feet per minute. The 16 filaments emerging from the spinneret were divided in the quench bath into two groups of eight (for making 50- to 55-denier oriented yarns) or into two groups of six (for making 40-denier oriented yarns) and a third of four filaments which was discarded. During the first few hours of yarn collection, the yarn was doffed every 15 minutes, then the collection time per package was increased to 45 minutes to make about 1-pound packages. A sample of yarn was taken from each package for measurements of filament uniformity and birefringence. Filament uniformity was measured in two ways. Sections were taken across the yarn sample in three locations and the diameters of the filaments in each section were measured with a microscope fitted with a Filar micrometer. In the absence of variations in diameter along the length of the filaments, this examination will disclose differences in the size or condition of the orifices. In the second method, specimens were taken at about 6-inch intervals along a 5 to 6 foot length of a single filament from the yarn and the diameters of these specimens were measured to detect variations in filament diameter. If the variation in diameter along the filament exceeded ±5% from the average the yarn was not considered satisfactory. Somewhat more variation was allowed in the diameters of the filaments in a cross section of the yarn but it was generally limited to ±10% for acceptance.

2. Orientation

The yarn-drawing equipment was arranged as described in Section A.2.b. and Figure 11 in the appendix. With this arrangement, the yarn was cold drawn between a feed godet and a heated godet located inside an 8-foot long oven and further drawn between the heated godet and a third godet (also heated) located near the exit from the oven.

The preferred conditions for drawing yarns spun under conditions considered optimum were: a 5X cold draw between the feed godet (at room temperature) and the second godet (at 135°C), and further drawing to an overall in this operation of about 7.7X) between the second godet and the final godet (at 135°C) with the oven at 135°C. The rate of drawing was 75-100 yards per minute at the final godet.

G. Properties of High-Tenacity Polypropylene Yarn

The properties of a high-tenacity polypropylene yarn, representative of those produced in this program, are given in Table V. These properties include the molecular characteristics of orientation, birefringence, refractive index, and crystallite orientation as well as the usual physical properties. High molecular orientation is the outstanding characteristic of high-tenacity polypropylene fibers, and accounts for their high strength. All of the values shown in Table V were obtained for filaments selected to have tenacities in the range of 13.0±0.3 g/denier.

Table V. Properties of Representative High-Tenacity Polypropylene Yarn

Tenacity, g/denier	12.9
Elongation at break, %	14
Initial modulus, g/denier	171
Energy of rupture, cm. g.	25
Knot strength, g/denier	7.4
Loop strength, g/denier	6.8
Molecular orientation	0.86
Density, g/cm^{-3}	
Refractive Index	1.504
Birefringence	0.037
Crystallinity fraction	
Crystalite orientation	
Hermans orientation factor	
P-axis	-0.49
C-axis	+0.98

The degree of crystallinity in these fibers was moderate and the crystallite orientation was high. The filaments had high modulus in extension indicating that they were comparatively stiff, since filaments having a high extension modulus generally have a high bending modulus. The knot and loop strengths of the filaments were substantially lower than the tenacity, which indicates that the fibers were brittle. These are characteristics that would be expected in high-tenacity fibers.

IV. INVESTIGATION OF METHODS OF PRODUCING COLORED HIGH-TENACITY POLYPROPYLENE FIBERS

A vat-dyed fabric matching the color of TCCA Cable No. 70068 was desired for construction of liferafts, but it was recognized that the prospects for producing a dyeable high-tenacity polypropylene fabric were not promising.

Two general techniques for making dyeable polypropylene fibers were available at the time this work was done. One of these involved adding a polymeric dye acceptor (e.g. poly(vinyl-pyridine)); the other, adding a metal salt to the polypropylene used for spinning the fibers. Salts of aluminum and of nickel were both being used commercially. Only the metal salt additives could be considered for our use, because it had already been established that high-strength polypropylene fibers could not be made from blends of polypropylene and the polymeric dye receptor.

A sample of a commercial polypropylene (Profax 6614) containing a proprietary nickel compound was obtained from Hercules, Incorporated. This polymer was being used for commercial production of dyeable polypropylene yarns. The Profax 6614 was melt spun under the general conditions established for melt spinning Profax 6723. Since the Profax 6614 had a higher Melt Index than Profax 6723, it was spun with slightly lower temperatures in the extruder than those used for Profax 6723 so that the extrudated polymer would have the desired 2.0 Extrusion Index. The melt-spun yarns of Profax 6614 were oriented under a variety of conditions, but the highest strength yarns that were produced had a tenacity of only 9 g/denier.

A study of the preparation of fibers from Profax 6723 containing 1% aluminum stearate was also carried out in the effort to make dyeable high-strength polypropylene fabrics. The mixtures of polypropylene and aluminum stearate were prepared by first milling together on a two-roll rubber mill a mixture of 10 parts of aluminum stearate and 90 parts of Profax 6723, granulating this milled mixture, and then blending 10 parts of these granules with 90 parts of Profax 6723. This blend, which contained 1% of aluminum stearate, was melt spun under the same conditions used to make high-tenacity yarns from Profax 6723 alone. The highest strength of yarns oriented under a variety of conditions was 8 g/denier.

These results indicated that it would not be possible to make high-tenacity yarns from polypropylene containing either the proprietary nickel salt dye acceptor or aluminum stearate, at least without extensive effort. Since it is known that metal salts can act as nucleating agents and promote crystallization before the high degree of orientation required could be attained.

Attempts were made to prepare dope-dyed high-tenacity polypropylene although it was anticipated that it was unlikely that satisfactory results would be obtained. Recommendations were obtained from several suppliers of dyes and pigments that were being used for dope-dyeing polypropylene. The choice of materials was limited because of the high temperatures used in our melt-spinning operations, but Hercules, Incorporated, was able to supply a pigment (dispersed in polypropylene) that was thermally stable. This dispersion was prepared so that a mixture of 1 part of the dispersion and 50 parts of clear polypropylene would have the color desired. Yarns were melt spun successfully from this mixture, but the highest tenacity that could be attained was about 9 g/denier.

The unsatisfactory results of these attempts to make dyeable or dope-dyed high-tenacity polypropylene yarns led to the conclusion that the liferaft fabric would have to be colored by pigmenting the coating only.

V. WEAVING OF FABRICS

All twisting of yarns for use in fabrics and all fabric weaving were done by Prodesco, Incorporated, Perkasie, Pennsylvania, under a subcontract with Southern Research Institute. None of these operations was witnessed by representatives of the Institute. The following discussions of the various operations are based on information obtained by correspondence and conversations with representatives of Prodesco. We understand that all warp yarns were twisted 4 TPI and all filling yarns 1.5 TPI.

Fabric Sample No. 4319-49-1 - This fabric was made as an initial trial to determine what problems might be encountered in weaving the high-tenacity multifilament yarns. About 3 sq yd of 24-inch 2/2 twill with 160 ends and 100 picks per inch was woven, and delivered to the Institute. Prodesco reported that twisting the yarns was difficult and that the maximum fabric weight attainable was 1.6 oz/sq yd, which was somewhat lower than the 2.0 oz/sq yd desired.

Unfortunately, Prodesco scoured this fabric in Varsol (a hydrocarbon solvent) and this treatment degraded the filaments. The strength of filaments taken from this fabric was only about 60% of the value when the yarns were shipped to Prodesco. The effect of Varsol on the strength of high-tenacity polypropylene filaments was verified in our laboratory by soaking filaments in Varsol for 3 hours and then allowing them to dry overnight. The strength of filaments treated in this way was approximately 60% of the original strength.

Fabric Sample No. 4319-49-1A - This fabric sample was prepared without the Varsol treatment to replace Sample 4319-49-1 discussed above. The twisting of the yarns presented less problems than in the previous operation, partially because an improved lubricant (Rohm and Haas Lubricant 3930) was supplied to Prodesco and partially because of the experience gained in the previous operation. This fabric, like the previous one, had 160 ends and 100 picks per inch, was a 2/2 twill construction, and weighed 1.6 oz/sq yd. Prodesco reported some difficulties in weaving this fabric because of filament breakage in the warp.

The breaking strength of this fabric was 110 lb/in. in the warp direction and 100 lb/in. in the filling direction. Although this breaking strength was below that specified in MIL-C-19377 for the neoprene-coated nylon life-raft fabric (160 lb/in. warp direction and 140 lb/in. filling direction) the strength was about what would be expected. With 160 ends of 40-denier yarn with filaments of 13 g/denier tenacity, the

sum of the breaking strengths of the filaments would be about 180 lb, and, similarly, with 100 picks of 55-denier yarn, the sum of the filament strengths would be about 160 lb. It is to be expected that the strength of a fabric woven of a high modulus and relatively brittle fiber will have an appreciably lower strength than the sum of the breaking strengths of the filaments.

This polypropylene fabric was relatively stiff and had poor hand and drape. These characteristics were the inevitable consequence of the stiffness of the high-tenacity polypropylene filaments.

From a practical standpoint, the difference between the strength of the polypropylene fabric and the specification strength of the nylon fabric is not as great as the above figures indicate. These strength values are for fabrics conditioned in air at 65% R.H., but, in actual use, much of the fabric in a liferaft will be wet with water. Specification MIL-C-19377 states that the nylon yarn used in the fabric shall be a high-tenacity multifilament nylon yarn but does not specify the tenacity. Published data[1] for one presumably typical high-tenacity nylon 66 yarn shows a tenacity (at 20°F) of 9.2 g/denier at 65% R.H. and a tenacity of only 7.4 g/denier when wet. If this 20% loss in yarn strength on wetting also occurs in the fabrics made from the yarn, as seems likely, the nylon fabrics having strengths of 160 lb/in. in the warp and 140 lb/in. in the fill directions at 65% R.H. would have corresponding strengths of about 130 lb/in. and 110 lb/in. when wet. The strengths of polypropylene yarns are, of course, unaffected by wetting. In view of these considerations, the strength of the polypropylene fabric was not unacceptable; and the program was continued.

Fabric Sample No. 4319-49-2 - Since Prodesco had reported difficulties in weaving Fabric Sample No. 4319-49-1A because of filament breakage in the warp, we supplied them with yarns having larger filaments than those in the yarns used in that sample. The warp yarn was a 4-filament 40-denier yarn and the fill yarn was a 5-filament 55-denier yarn. Prodesco wove 3 yards of 24-inch fabric with a 2/2 right-hand twill construction with 160 ends x 100 picks from these yarns, and reported that they encountered no difficulties in twisting or weaving, either with the warp or the filling yarn. The weight of the fabric was 1.60 oz/sq yd. Apparently these yarns with 10 or 11 denier

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1. E. I. du Pont de Nemours and Company, Inc. Bulletin X-188 - Physical and Thermal Properties of Du Pont Industrial Yarns.

filaments were more resistant to the wear-and-tear of the twisting and weaving operations than were the yarns used in the previous trials which had 6-7 denier filaments.

The breaking strength of this fabric was 120 lb/in. in warp direction and 100 lb/in. in the fill direction. The strength of this fabric was slightly better in the warp direction than that of Fabric Sample No. 4319-49-1A, probably because of less yarn damage during twisting and weaving, but this fabric was noticably stiffer than Fabric Sample No. 4319-49-1A. This disadvantage, resulting from the larger filament size, offset the improved ease of processing.

Fabric Sample No. 4319-49-3 - This sample was made from the same yarns used to make Fabric Sample No. 4319-49-2, but it had a basket weave rather than 2/2 twill construction. Approximately 3 sq yd of 24-in. fabric was woven with 160 ends and 100 picks. The weight was 1.6 oz/sq yd. It was hoped that the basket-weave construction would result in a more flexible fabric than the twill construction, but the difference in flexibility was not great enough to constitute a significant advantage for the basket weave.

The breaking strength of this fabric was 85 lb/in. in the warp direction and 105 lb/in. in the fill direction.

Fabric Sample No. 4319-49-4 - This sample was 48 in. wide and about 95 sq yd was produced. The fabric construction was 2/2 right-hand twill with 160 ends and 100 picks. The weight was 1.6 oz/sq yd. The breaking strength of the fabric was 120 lb/in. in the warp direction and 115 lb/in. in the fill direction.

Prodesco reported that they had considerable difficulties in making this sample. We were informed that numerous filaments broke during twisting, and, as a result, there were broken filaments in the beamed warp; also that additional filament breakage occurred during weaving, which was not surprising since the warp was not sized. We are not certain of the relative severity of the problems in twisting and in weaving, but we received the impression that the major difficulty was in the twisting.

Despite these reported difficulties, 95 sq yd of fabric of acceptable appearance was woven.

Fabric Samples No. 4319-49-5, -6, -7, -8, and -9 - Because of these difficulties experienced in preparing Fabric Sample No. 4319-49-4, the yarns supplied for the fabrics of this series were carefully inspected before shipment to Prodesco. Since twisting of the yarns had been a source of difficulty in the

preparation of Fabric Sample No. 4319-49-4, a study was made of the twisting of these yarns. It was found that they could be twisted without difficulty in a down-twister if a traveler of the proper size was used and if the yarn was well lubricated with Rohm and Haas Lubricant 3937. It was necessary to use a traveler of the lightest weight that would give satisfactory twisting. We supplied Prodesco with specific details of the procedure developed in our laboratory for twisting the yarns and they reported that the twisting of these yarns was accomplished without difficulty in their plant.

When the warp yarns were beamed, more slubs were found than had been anticipated but these were carefully removed and Prodesco reported at that point that they did not expect to encounter the difficulties in weaving these yarns that they had experienced in weaving Fabric Sample No. 4319-49-4.

About 1 yd of 48-inch 2/2 twill (Sample No. 4319-49-5) was woven, apparently without difficulty. However, Prodesco advised us at this point that they would not be able to complete the weaving with the funds available. This situation was discussed with representatives of NASA, and it was decided that the remainder of the yarn should be woven into a fabric with a rip-stop construction for use as parachute fabric.

There was delay in obtaining final authorization to proceed with preparation of the rip-stop construction, and still further delay because of lack of availability of equipment at Prodesco so that the warp yarn was stored on the beam for a period of nearly 4 months. When weaving was resumed Prodesco reported great difficulty in the operation. Filament breakage in the warp was so great that even with constant operator attention the weaving rate was very slow. It appeared that the warp yarn had deteriorated during the long storage, but this was not proven. Our inspection of this yarn, Prodesco's experience in twisting the yarn, and the results of the initial weaving trial before the long storage period all indicated that this yarn was superior to that used in preparing Fabric Sample No. 4319-49-4, and, other than deterioration, there is no reasonable explanation of why it should have been more difficult to weave this yarn than it was to weave the yarn used in Fabric Sample No. 4319-49-4.

Prodesco discussed the difficulties they were encountering with a representative of NASA and were authorized to terminate the weaving. The yarn on the beam was discarded, since it could not be recovered in useful form, and all other yarn was shipped to NASA, attention of Mr. Jack Naimer.

A listing of the fabric samples woven by Prodesco is given in Table I. Fabric Samples 4319-49-1A, -2, -3, and -5 were delivered to Southern Research Institute and were used in the studies of fabric properties and in studies of coatings. Fabric Sample 4319-49-4 was divided into several portions — the major portion (75 to 80 yd) was delivered to Fabrics Research, Inc. and a few small samples (the size of which was not recorded) were sent by Prodesco to several fabric finishers who used them to investigate the feasibility of priming the fabric in their facilities. About 15 yards of Sample 4319-49-4 was received by the Institute, and, of this, 9 yards was used in the investigation of coatings, 3 yards was sent to Thiokol for use in their study of carboxy nitroso rubber (CNR) coatings, and 3 yards was sent to Alden Rubber Company for coating experiments.

VI. INVESTIGATION OF POLYURETHANE COATINGS

At the start of this phase of the program, requests for recommendations regarding polyurethane coating materials that would meet the requirements for the liferaft fabric were sent to 12 manufacturers of polyurethane materials. The response to these inquiries was good, but none of those replying supplied any data to indicate that the coating materials they could offer would meet the requirements.

To gain additional information, telephone calls were made to several of the suppliers of coating materials and a visit was made to Aldan Rubber Company who have had considerable experience in coating fabrics. None of these companies had had any experience in applying polyurethane coatings to polypropylene fabrics. We did, however, find considerable information on polyurethane coatings for other types of fabrics, particularly nylon. These contacts indicated that the type of polyurethane most commonly used for fabric coating was the soluble-gum type. This type of material can be applied either as a solution, with conventional knife-coating equipment, or as sheets of the gum, which are applied by calendering them onto the fabric. We found that moisture-cured polyurethanes were being used to a limited extent, but primarily as carpet or fabric backing where it was not necessary to have the coating free of pinholes. Chemical-curing types of polyurethanes appeared to be little used as fabric coatings. In fact, the only example found of the use of this type was on a coated webbing being made by the Navy.

On the basis of this survey of the state of the art of polyurethane fabric coatings, it appeared that the soluble-gum type of polyurethane was the most desirable, particularly because it was the only type that could be applied with conventional equipment. Our main efforts with coatings were, therefore, made with this type of coating material, but brief trials were made with chemical-curing, moisture-curing types.

A list of the coating materials that were examined in this program and their sources are given in Table VII in Section B-2-a of the appendix.

A. Soluble-Gum Polyurethanes

1. Estane coatings on untreated fabric

The Estane polyurethanes offered by B. F. Goodrich were representative of the soluble-gum type of coating materials. Three Estane polymers, identified as 5701, 5702, and 5710, that differed in molecular weight were tried as coatings for polypropylene fabrics. Solutions of these polymers in tetrahydrofuran were applied to samples of the fabric with a doctor blade and the solvent was removed by placing the coated fabrics in an oven at 50°C for 1 hour. These materials were easy to apply and coatings of excellent appearance were obtained. However, the bonding of the coatings to the polypropylene fabrics was unsatisfactory for each of the three coatings, being only about 6 lb/in.—about half of that required.

In attempts to improve the bonding of the coating to the fabric, we investigated the effectiveness of several priming treatments. Of the three Estanes, 5710 would probably be the most desirable because it had the highest molecular weight, which should result in the toughest coating. Hence, Estane 5710 was used in the study of primers.

2. Primers for Estane coatings

A review of the literature and contacts with industry representatives disclosed many suggested primer treatments for polypropylene but few of these appeared to be practical for priming fabrics for coating. The materials selected for investigation as primers and the sources of those that are proprietary materials are given in Table VIII in Section B-2-b of the appendix. The results of experiments to evaluate these treatments are summarized in Table VI.

a. Polymethylene polyphenylene isocyanate primer

A solution for priming polypropylene fabric was prepared by dissolving 25 parts of polymethylene polyphenylene isocyanate (Cargin Chemical Company) in 75 parts of 2-butanone. Samples of polypropylene fabric were dipped in the solution, allowed to drain, air dried for 10 minutes, and then dried in an air-circulating oven at 80°C for 30 minutes before coating them with Estane 5710 as described in Section VI-A-1. Coatings of both 20 and 25% solutions of Estane 5710 were applied to fabric samples primed with polymethylene polyphenylene isocyanate.

Table VI. Bond Strengths of Estane 5710 Coatings Applied to Polypropylene Fabrics Treated with Various Primers

Sample 4316-	Primer	Adhesion strength lb/in.[a]
9-1	None	6
10-1	25% Polymethylene polyphenylene isocyanate in 2-butanone	6
27-2	10% Aluminum chloride in tetrachloroethylene	8
19-1	Thixon XAB-936	4
19-2	Thixon XAS-166	6
19-3	Thixon XAB-1089	6
19-4	Thixon XD-738/Thixon XD-6763	1
27-3	20% Chromyl acetate	7
23-1 and -2	5% Di-n-butyl monophosphoric acid in methyl ethyl ketone	15

a. Average for 3 or more determinations.

No increase in the bond strength of the coating, in comparison with a similar coating on untreated fabric, resulted from the priming treatment.

b. Aluminum chloride primer

An aluminum chloride primer solution was prepared by suspending 10 parts of aluminum chloride in 100 parts of tetrachlorethylene. The suspension was heated to 50-55°C and a sample of polypropylene fabric was immersed in the suspension for 5 minutes while it was stirred. The sample was then washed, first in cold water and then in hot water, and then it was dried at 100°C for 5 minutes. The specimens were washed, dried, and coated with a 25% solution of Estane 5710.

This priming treatment increased the bond strength between the coating and the fabric from 6 lb/in. (for unprimed fabric) to 8 lb/in.—still well below the desired 12 lb/in.

c. Thixon primers

Samples of polypropylene fabric supplied by us were primed by Dayton Chemical Products Laboratories with four agents. The reported treatment for each sample was as follows: (1) sample was treated by dipping it in Thixon XAB-936, which had been diluted with an equal amount of 2-butanone (Sample 4316-19-1); (2) sample was treated with Thixon XAS-166 primer (Sample 4316-19-2); (3) sample was treated with Thixon XAB-1089 primer (Sample 4316-19-3); and (4) sample was first treated with Thixon XD-7538 diluted 1:1 with heptane, allowed to dry, and then treated with a mixture of Thixon XD-6763 diluted 1:1 with a toluene/2-butanone mixture (Sample 4316-19-4). Each of the primed samples was coated at the Institute with a 20% solution of Estane 5710 and cured according to the procedure described earlier.

The bonding of the coatings to the treated fabrics was no better than to untreated fabric.

d. Chromyl acetate primer

A chromyl acetate solution was prepared containing 20 g of chromium trioxide in 100 g of acetic anhydride. The materials were stirred at room temperature and filtered to remove any undissolved material. Samples of polypropylene fabric were

soaked in the solution for 5 minutes and then allowed to air dry for about 2 hours before coating with a 20% solution of Estane 5710 and curing, as described in Section VI-A-1. Only a slight improvement in the bonding of the coating to the fabric (from 6 to 7 psi) resulted from pretreating the fabric with chromyl acetate.

e. Di-n-butyl monophosphoric acid primer

A sample of polypropylene fabric was soaked in a 5% solution of di-n-butyl monophosphoric acid in ispropanol for about 5 minutes, then it was allowed to drain and air dry. Then it was heated in an oven for 15 minutes at 80°C while stretched on a tenter frame. The treated fabric was then coated with Estane 5710 and cured as described above. The bond strength was 15 lb/in.

Di-n-butyl monophosphoric acid was the only primer among those investigated that gave sufficiently improved bonding to satisfy the requirements of 12 lb/in. minimum bond strength. Since the treatment with di-n-butyl monophosphoric acid was simple and effective, no further search for primers was made.

3. Estane coatings on primed fabric

Coatings of Estane 5710 were applied to 1.6-oz 2/2 twill fabric primed with di-n-butyl monophosphoric acid as described in Sections VI-A-1 and -2-e. Coating weights were 2 to 3 oz/sq yd.

The blocking resistance of these coatings was rated as Grade 4, which indicated a much greater tendency to block than desired (Grade 2 or less). The abrasion resistance of the coated fabric was only about 175 cycles, which is well below the 1500 cycles required to induce failure in the present neoprene-coated nylon when tested under identical conditions. The poor abrasion resistance of these coated fabrics appeared to be a result, primarily, of the poor abrasion resistance of the high-tenacity polypropylene fabric. The 1.6-oz fabric of high-tenacity polypropylene is far less resistant to abrasion than the approximately 4.5-oz nylon fabric, and the major contribution to the abrasion resistance of the coated nylon fabric comes from the fabric rather than the neoprene coating.

The difference in the behavior of the polypropylene and nylon fabrics when subjected to the Taber Abrasion Test with H-18 wheels was pronounced. When abraded on the fabrics side, about 200 cycles was required to wear away the polypropylene fabric and when the coating was exposed, it was snagged and torn by the rough H-18 wheel. About 1200 cycles was required to wear through the nylon fabric and expose the neoprene coating, and again when the coating was exposed it was torn and failure occurred quickly. When the coated polypropylene fabric was abraded on the coated side, failure occurred very soon after the coating was worn away. As soon as the coating was gone, the H-18 wheels snagged the filaments in the fabric and small holes appeared. The polypropylene made a negligible contribution to the abrasion resistance measured under these conditions. In contrast, the fabric was a major contributor to the abrasion resistance of the coated nylon fabric. The neoprene coating was worn away in 200-400 cycles, but an additional 1000-1200 cycles was required to cause failure of the fabric.

In service, the fabric side of the fabric would be subjected to more abrasion than the coated side, so the relative abrasion resistances of the fabrics are probably more significant in regard to performance in service than the abrasion resistance of the coatings.

The relatively poor abrasion-resistance of the high-tenacity polypropylene fabric is caused by several factors. This fabric is much lighter than the nylon fabric (1.6 vs 4.5 oz/sq yd). The filaments in the polypropylene fabric are much larger than those in the nylon fabric and, even if all else had been equal this would have detracted from the abrasion resistance of the polypropylene fabric. The major factor is probably the low abrasion resistance of the high-tenacity polypropylene filaments, which is appreciably less than that of commercial polypropylene filaments of 5-7 g/denier tenacity. Several attempts were made to obtain precise comparisons of the abrasion resistances of high-tenacity polypropylene filaments and polypropylene filaments of comparable size having 7 g/denier tenacity. The precision of measurements was poor, but it was established that the abrasion resistance of the high-tenacity polypropylene filaments was between 50% and 75% of that of the 7 g/denier filaments.

This type of soluble-gum polyurethane probably would be the best choice for coated polypropylene fabrics. This type can be easily applied, and Aldan Rubber successfully coated some high-tenacity polypropylene fabric with Impranil C* in pilot-scale equipment. However, work on the program was discontinued before plant-scale coating trials were made.

4. Elastothane coatings

Thiokol Chemical Company had developed a sulfur-vulcanizing soluble-gum polyurethane (Elastothane) which was of interest because of its high tensile strength and good abrasion resistance when cured. Thiokol supplied a compounded stock of undisclosed composition. A solution of this stock in methyl ethyl ketone (MEK) was applied to polypropylene fabric, and, after the solvent had evaporated at room temperature, the coated fabric was stretched on a tenter frame and placed in an oven at 125°C to cure the coatings. Curing was carried out at this temperature for times of 30, 60, 90, and 120 minutes. Observations of the extent of swelling of the coatings when the coated fabrics were immersed in MEK indicated that curing was not complete in 120 minutes.

A second sample of Elastothane compounded by Thiokol with a modified curing system had somewhat better curing properties, but about 3 hours at 125°C was required to obtain what was considered satisfactory curing. The bonding of a 2.5 oz/sq yd coating of this Elastothane of polypropylene fabric primed with di-n-butyl monophosphoric acid was satisfactory (about 15 lbs/in.). The blocking resistance was satisfactory, but the abrasion resistance of the coating was only 220 cycles.

The coatings of Elastothane were somethat superior to those of Estane 5710 in abrasion resistance and in resistance to blocking, but the long curing time at 125°C was undesirable.

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* Impranil C is a soluble-gum type of polyurethane sold Verona Chemical Company.

B. Chemical-Curing Polyurethanes

The incentive to investigate chemical-curing polyurethanes was that these offered a way to obtain coatings of higher abrasion resistance than coatings of the gum elastomer type. The chemical-curing type of polyurethane is, as was indicated earlier, little used for fabric coating, probably because it is not easily applied with conventional fabric coating equipment.

Only one of the suppliers contacted, the Bostick Division of United Shoe Machinery Corporation, offered to supply materials of this type. These, together with coating materials based on Adiprene L-100 from Du Pont and prepared at the Institute, were investigated.

1. Bostick Yellow coatings

Preliminary experiments with two chemical-curing polyurethanes supplied by United Shoe Machinery Corporation (Bostick S175-1021 and -1084) showed that films with maximum tensile strength were obtained with mixtures of about 12 parts of prepolymer and 1 part of curing agent (Boscodur #1), and that a curing time of about 90 minutes at 100-110°C was required for full curing.

Coatings on polypropylene fabric were made with compositions prepared by mixing 12 parts of prepolymer with 1 part of Boscodur No. 1 and 3 parts of 2-butanone. The coatings were cured under the conditions given above. The coating of S175-1021 was very inflexible after curing and was judged unsatisfactory without further evaluation. The coating of Bostick S175-1021 was satisfactory in flexibility and in appearance and was studied further.

Coatings of Bostick S175-1021 adhered well to polypropylene fabric primed with di-n-butyl monophosphoric acid. Bond strengths between coating and fabric in the range of 20-25 lb/in. were obtained. The abrasion resistance of 2.5 oz/sq yd coatings of S175-1021 was about 175 cycles, and the blocking resistance was Grade 4 both of which were unsatisfactory. The coatings of this polyurethane appeared to offer no advantages over the Estane coatings.

Mixtures of S175-1021 and S175-1084 were investigated to determine if improved coatings could be obtained. It was found necessary to have about 50% of the S175-1084 in the mixture to obtain coatings having satisfactory resistance to blocking, and, with this level of S175-1084, the coatings were quite stiff and the abrasion resistance was only 200 cycles. Work with these coating materials was discontinued.

2. Adiprene L-100 coatings

A review of published literature on the abrasion resistance of a variety of polyurethanes showed that those prepared by curing Adiprene L-100, an isocyanate-terminated prepolymer manufactured by Du Pont, with MOCA [4,4'-methylene bis(2-chloroaniline)] had outstanding resistance to abrasion. Although it was recognized that these coatings would be stiffer than desired, the prospect of obtaining high resistance to abrasion encouraged investigation.

Coating compositions were easily prepared by mixing the Adiprene L-100 with MOCA dissolved in methyl ethyl ketone and then diluting the mixture to the desired viscosity with the solvent. The preferred composition was a mixture of 100 parts of Adiprene L-100 and 13 parts MOCA dissolved in MEK. A problem with this type of coating composition is that reaction begins as soon as the Adiprene L-100 and MOCA are mixed and the viscosity of the solution increases rapidly. The best procedure for laboratory coating applications involved preparing solutions much lower in viscosity than desired, waiting until the viscosity increased to the desired level, and then applying the coating as rapidly as possible. This was not entirely satisfactory and the yield of good coatings was low.

The coatings of Adiprene L-100 and MOCA required curing for 3 hours at 100°C. The fully cured coatings had excellent abrasion resistance. The abrasion resistances of samples with coating weights of about 2.5 oz/sq yd were in the range of 400-700 cycles. The variation resulted in part from variation in the viscosity of the coating material at the time of application. When the viscosity of the solution was a little lower than optimum, more of the coating material penetrated into the yarn and was less effective for providing abrasion resistance than when the coating remained on the surface of the fabric.

Although the coatings of Adiprene L-100 cured with MOCA had the exceptionally high abrasion resistance desired and they bonded well to the polypropylene fabrics primed with di-n-butyl monophosphoric acid, the coatings were not as flexible as desired, and it would have been a formidable task to apply them on a plant-scale.

C. Moisture-Curing Coatings

Moisture-curing polyurethanes are isocyanate-terminated prepolymers. When films of these are exposed to the moisture that is normally present in the atmosphere, reaction occurs and "curing" takes place. Carbon dioxide is generated during the curing and, unless the conditions of cure are such that the carbon dioxide can diffuse out, pin holing or even foaming will occur. For this reason moisture-curing polyurethanes were not considered suitable for the abrasion-resistant coating on the fabrics.

However, a thin colored coating was required on the back of the fabric, since it was not possible to make a dyeable or a dope-dyed high-tenacity polypropylene fabric and the moisture-curing polyurethanes were of interest for providing a colored coating.

Nopco Chemical Company supplied three materials of the moisture-curing type and preliminary evaluations indicated that Nopcobond SX-159-D was the most promising of the three.

A colored coating composition was prepared by stirring Ferro-971 yellow, a pigment dispersion supplied by Ferro Corporation, into the Nopcobond SX-159-D, and diluting the mixture to the desired viscosity with 2-butanone. All mixing was done in a dry atmosphere.

This color coat could be applied to the back side of the fabric by brushing or spraying. Coating weights of 0.3-0.4 oz/sq yd were adequate to provide good hiding power.

VII. ADHESIVES

Little effort was required to find satisfactory adhesives for the construction of liferafts. Two types of adhesive compositions were tried—one was a conventional polyurethane gum mixed with a diisocyanate, and the other was a moisture-curing type.

The polyurethane-gum adhesive consisted of 100 parts of Estane 5710 and 15 parts of methylene bis(4-phenylisocyanate). The Estane 5710 was dissolved in methyl ethyl ketone (30-40% concentration was found to be a workable range), and the methyl bis(4-phenylisocyanate) was also dissolved in methyl ethyl ketone (50%). The two solutions were mixed to form the adhesive. The mixture thickened on standing but the pot life was at least 8 hours. The adhesive could be applied by brushing it onto the surfaces to be bonded and, after the major part of the solvent had evaporated, the pieces could be joined. This adhesive cures rather slowly by reaction of the diisocyanate with the active hydrogens in the polymer. Three to four days are required for "complete" cure. All of the adhesive bonding envisioned would be between polypropylene fabrics coated with polyurethane, and this adhesive provided stronger bond-between the polyurethane coatings than the bonds between coatings and fabric. This was verified with coatings of Estane 5710, Adiprene L-100 cured with MOCA, and moisture-cured Nopcobond SX-159-D.

The moisture-curing adhesive was a mixture of DDI, a diisocyanate derived from dimer acid, and an amine complex designated as Modified Amine 100. Both products were supplied by General Mills, Inc. This mixture was stable as long as it is protected from water. Water liberates the amine which then combines with the diisocyanate. This adhesive was selected for adhesive bonding nylon bias tape to polyurethane-coated polypropylene fabrics. The water absorbed in the nylon is sufficient to initiate the curing of this adhesive. Bonds between nylon bias tape and polyurethane-coated polypropylene fabric with this adhesive were stronger than the bonds between the coating and the fabric.

ACKNOWLEDGMENT

Mr. W. Curtis Stoner, assisted by technicians, carried out the experimental work concerned with developing the process for making the high-tenacity polypropylene yarns and preparing the yarns used in preparation of fabrics. Mr. Hollis H. Hill was responsible for determining the properties of the yarns. Dr. Edward R. Covington carried out the investigation of coating materials.

The cooperation and counsel of Dr. Frederick Dawn and Mr. Jack Naimer of NASA is gratefully acknowledged.

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October 15, 1968
9308-1694-XXXIX
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APPENDIX

EQUIPMENT, MATERIALS, AND PROCEDURES

A. Equipment

The major items of specialized equipment used in this program are described below. The standard testing equipment that was used is not listed.

1. Equipment for the preparation of yarns

a. Melt-spinning equipment

The melt-spinning equipment used in this program consisted essentially of a screw extruder equipped with a spinning head containing a gear pump for pumping the molten polymer through a filter pack and a spinneret, a water bath for cooling the extrudate, a twin godet take-up to draw the extruded filaments fron the spinneret at a controlled rate, and a winder. A schematic layout of the arrangement of the equipment is shown in Figure 9.

(1) Extruder

The extruder used in this program was purchased from Killion Extruders, Incorporated, Verona, New Jersey. It had a 1-inch-diameter barrel and a nylon type screw with a 20:1 length to diameter ratio. The extruder had two heating zones—the feed zone and the metering zone—and the temperatures in these zones could be controlled independently. The temperatures were monitored by a recording potentiometer with thermocouples in the feed and metering zones of the extruder.

(2) Spinning head

The spinning head was constructed in the Institute's shop; the design is shown in Figure 10. The spinning head and the Zenith metering pump were surrounded by an electrically heated aluminum block. Temperatures were monitored by a recording potentiometer with thermocouples in the top and bottom portions of the spinning head.

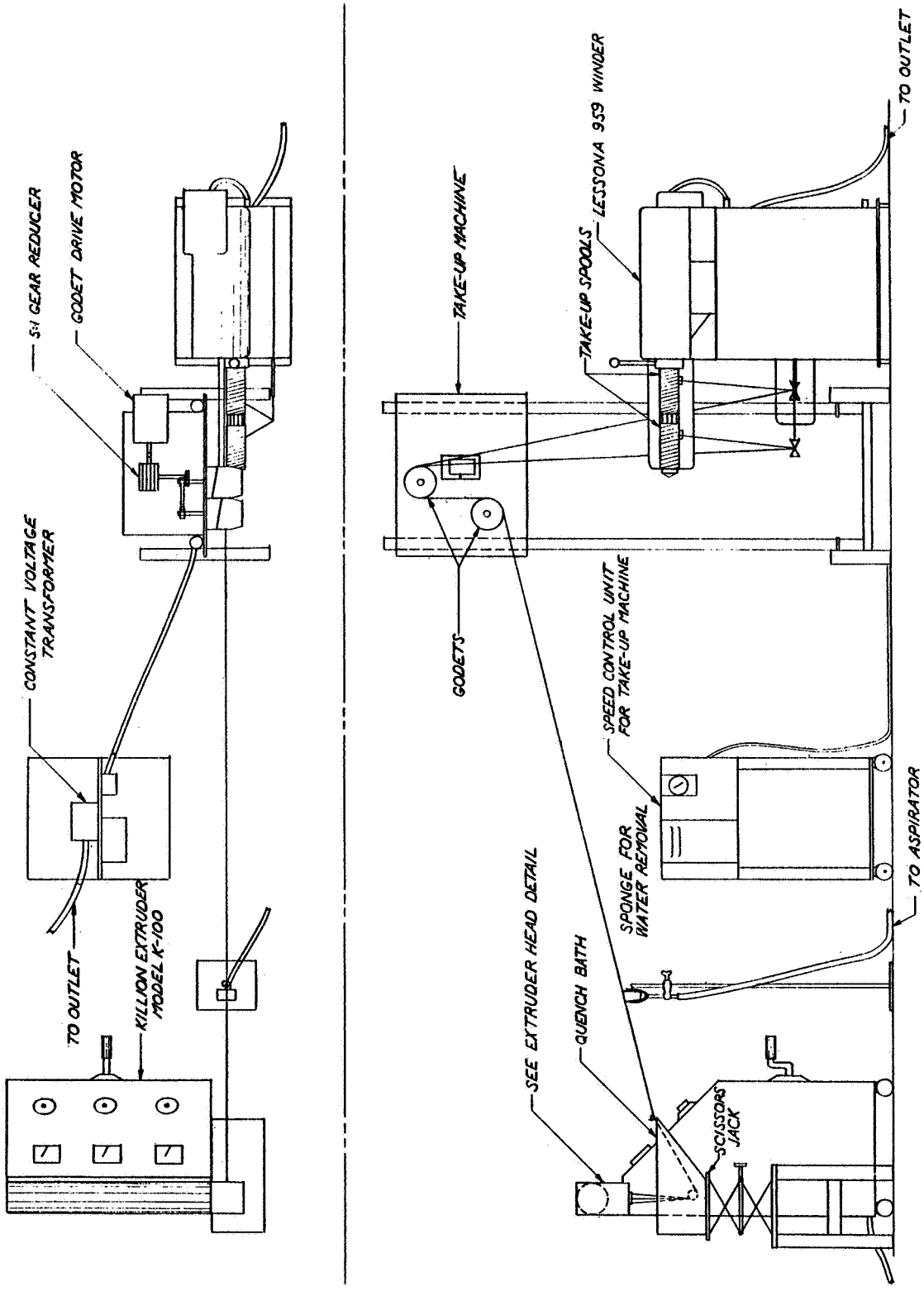

Figure 9. Equipment and Arrangement for Melt-Spinning Polypropylene Yarn

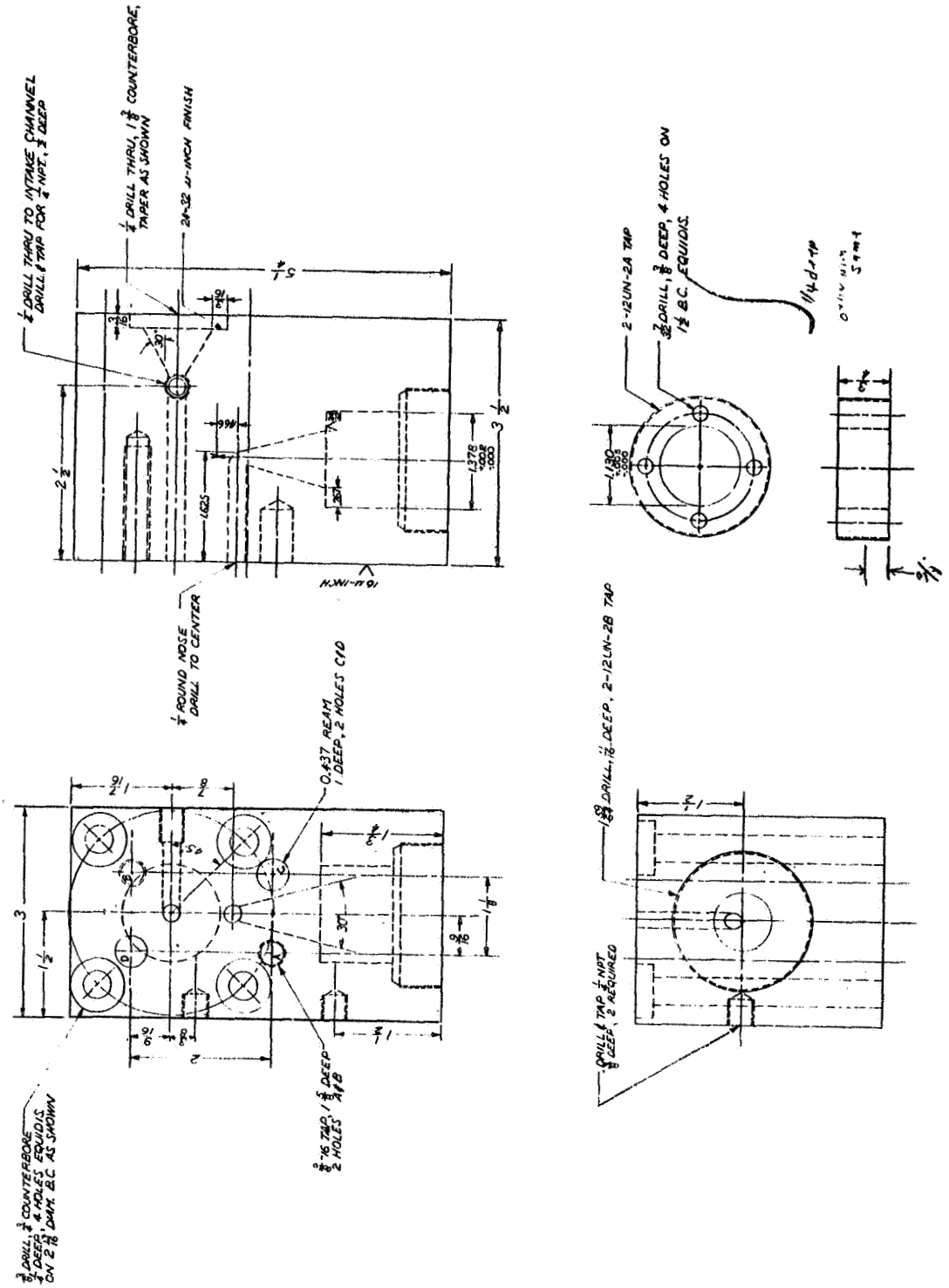

Figure 10. Details of Spinning Head

(3) Spinnerets

The type of spinneret used for the preparation of most of the polypropylene yarns for the production of fabrics had sixteen orifices, each 12 mils in diameter and with a length to diameter (L/D) ratio of 12:1 and a 40° entrance angle.

(4) Take-up

The yarn take-up equipment was constructed in the Institute's shop, but is of conventional design. The two godets (nominal 6-inch diameter) were driven at the same speed by a variable speed motor, operating through a timing-belt drive system.

(5) Winder

The spun yarns were wound onto tubes with a two-cop Leesona Model 959 Winder.

b. Machine-drawing equipment

The machine-drawing equipment used in the preparation of most of the yarns for weaving is shown in Figure 11. This equipment consisted of a 3-inch-diameter feed godet operating at room temperature, a second heated godet (Barber-Coleman) located inside an 8-foot-long electrically heated oven, and a third heated godet (Barber-Coleman) located outside the oven. The yarns drawn with this equipment were wound onto tubes with a single cop Leesona Model 950 Winder.

The following were also used for drawing in some experiments: (1) a 22-inch-long electrically heated aluminum shoe located between a 3.75-inch-diameter feed godet operated at room temperature and a 3.81-inch-diameter Barber-Coleman heated godet, (2) two 3.81-inch-diameter Barber-Coleman heated godets, (3) an 8-foot-long electrically heated drawing oven located between a 3.75-inch diameter godet operating at room temperature, and a 3.81-inch diameter Barber-Coleman heated godet, (4) a 10-foot-long, electrically heated, three-line, drawing oven. The 10-foot oven had three feed godets located outside the oven, a second set of three godets located about 9 inches inside the entrance ports, and a third set of three

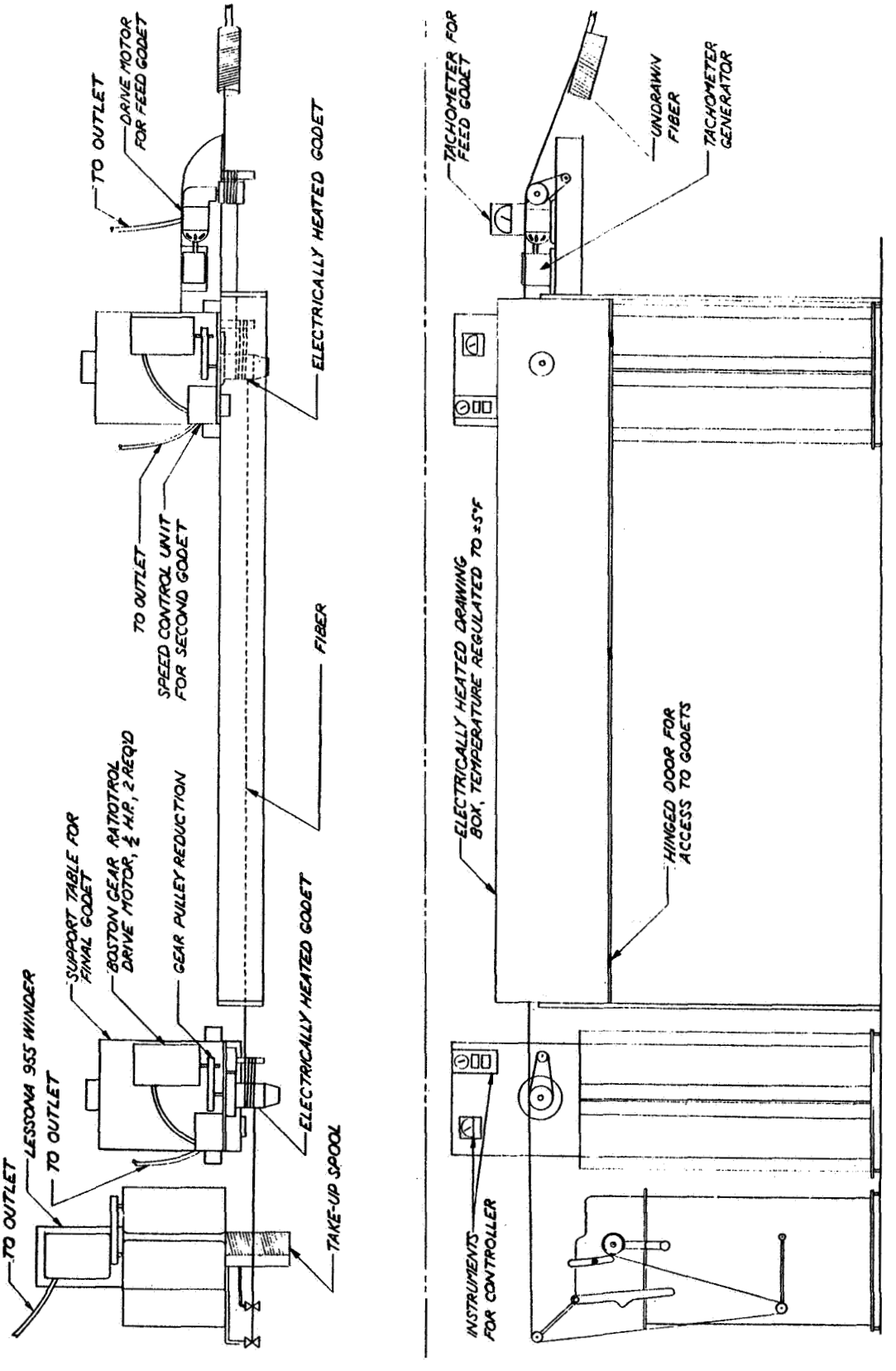

Figure 11. Equipment for Drawing Polypropylene Yarn

godets located about 9 inches from the exit ports. Each set of godets was driven by a variable-speed motor operating through a timing-belt drive system. All godets were 3.75-inches in diameter.

The yarns drawn with the three-line drawing equipment were collected on a single cop Model 950 and a two-cop Model 959 Leesona Winder. Yarns drawn on the other drawing equipment dexcribed above were located on a single cop Model 950 Leesona Winder.

c. Yarn twister

The yarn twister used in this program was a single-end down-twister manufactured by U. S. Textile Machinery Company.

d. Cone winder

Polypropylene yarns were wound on cones with a Model 50 Leesona Winder.

2. Equipment for melt-viscosity determinations

The melt viscosity of polypropylene was measured with a modified Slocum Melt Indexer set up as shown in Figure 12. The modification of the equipment consisted of attachment of a linear potentiometer to the piston of the melt indexer so that piston travel as a function of time could be recorded with a recording millivoltmeter.

B. Materials

1. Materials for fiber production

a. Polypropylene

The polypropylene used for the preparation of all high-tenacity yarns for weaving fabrics was Profax 6723. Two additional polypropylenes—Profax 6323 and 6623—were used in the experimental studies. The polypropylenes were all products of Hercules, Incorporated.

b. Yarn lubricant

The yarn lubricant used in most of our studies was prepared by mixing 9 parts of Lubricant 3930 with 1 part of Triton X-100 (both supplied by Rohm and Haas) and adding this mixture to 10 parts of water with sufficient stirring to form a stable emulsion.

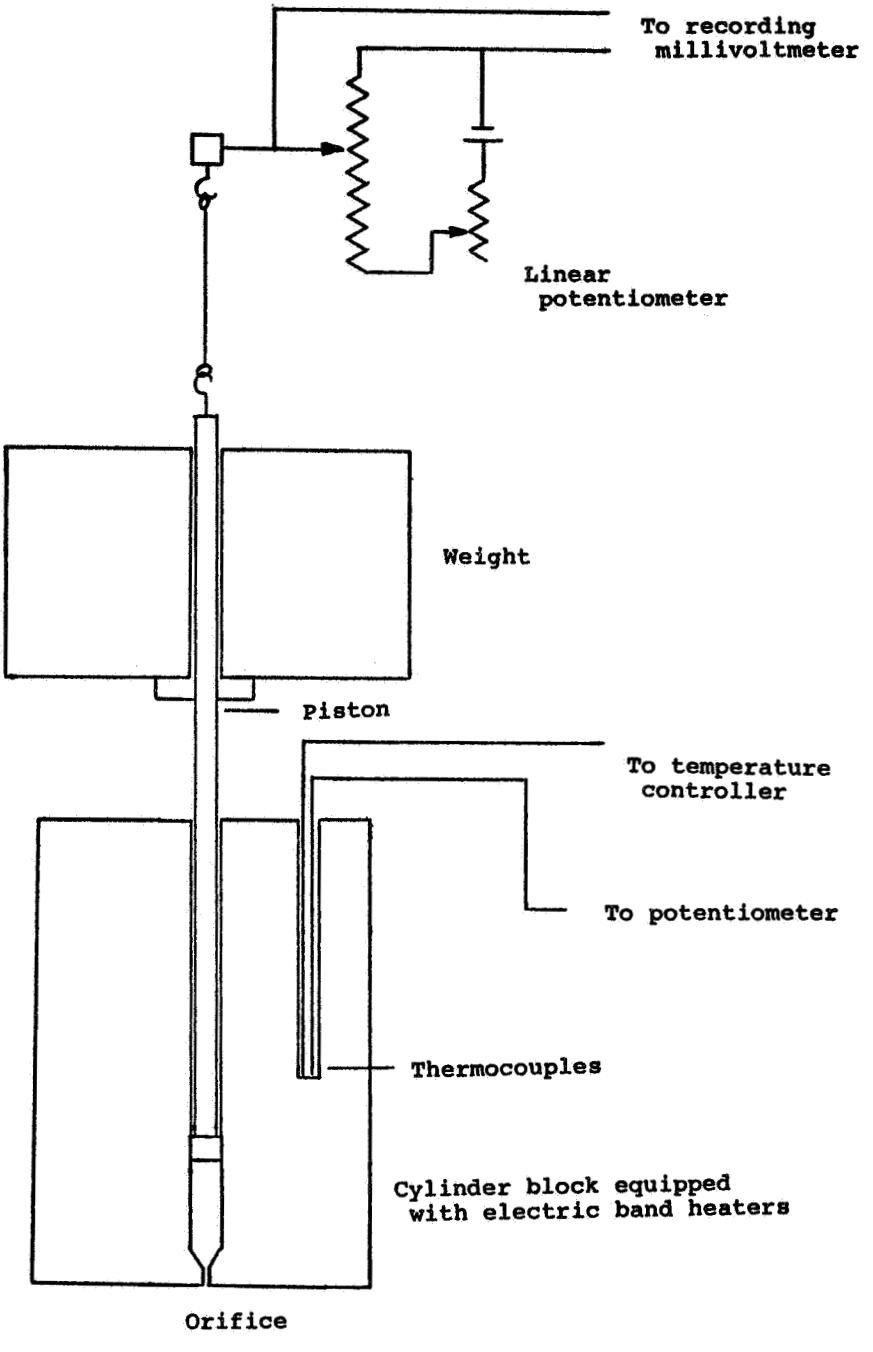

Figure 12. Schematic of Modified Melt Indexer

c. Wetting agent

Rohm & Haas Triton X-100 (about 1 ml/gallon) was used in the water quench to reduce the surface tension and prevent fusion of the multifilament yarns.

2. Materials for coating and treating fabrics

a. Coating materials

The materials used in the preparation of coatings for polypropylene fabric are listed in Table VII.

Table VII. Polymer Compositions and Pigment for Coatings

Polymer compositions	Source
Estane 5701 polyurethane	B. F. Goodrich Chemical Company
Estane 5702 "	" " " " "
Estane 5710 "	" " " " "
Adiprene L-100	E. I. duPont deNemours and Co., Inc.
MOCA [4,4'methylene bis(2-chloroaniline)]	" " " " " " "
Bostik Yellow S175-1021	United Shoe Machinery Corporation
Bostik Yellow S175-1084	" " " "
Boscodur #1	" " " "
Elastothane	Thiokol Chemical Corporation
Nopcobond SX-159-D	Nopco Chemical Corporation

Pigment	Source
Ferro 971 Yellow	Ferro Corporation

b. Primers

The materials used as primers on polypropylene fabric are listed in Table VIII.

Table VIII. Materials Used as Primers for Coatings

Primers	Source
Polymethylene polyphenylene isocyanate	Cargin Chemical Co.
Aluminum chloride	- - -
Thixon XAB-936	Dayton Chem. Prods. Labs
Thixon XAS-166	" " " "
Thixon XAB-1089	" " " "
Thixon XD-7538	" " " "
Thixon XD-6763	" " " "
Chromylacetate	- - -
Di-n-butyl monophosphoric acid	- - -

C. Procedures

1. Measurement of properties of yarns and filaments

a. Denier

Yarn deniers were determined by measuring 100-yard lengths of yarn with a Suter skein winder, weighing this length of yarn, and calculating the weight of 9,000 meters (denier). Filament deniers were measured with a Vibroscope according to method A of ASTM D1577-64T.

b. Tenacity

(1) Tenacity of twisted yarn

The tenacity of twisted yarn was measured by test method ASTM D1578-64T. The test equipment was a Model TM Instron Tester equipped with pneumatic clamps. The initial clamp separation distance was 10 inches and the separation rate was 5 in./min. The breaking strength of the yarn (in grams) was divided by the denier (determined by weighing 100 yards of yarn) to obtain the tenacity in grams per denier.

(2) Tenacity by single-filament method with denier determined by weight

By this method, tenacity of polypropylene yarn was determined by the procedure of ASTM D2256-64T with the yarn denier determined by weight. The breaking strength of each filament in a cross section of yarn was determined with a Model TM Instron with an initial clamp separation distance of 1 inch and a separation rate of 2 in./min. The total of the breaking strengths of the filaments in a cross section of yarn (in grams) was divided by the denier (determined by weighing 100 yards of yarn) to obtain the tenacity in grams per denier.

(3) Tenacity by single-filament method with denier determined with a Vibroscope

By this method, the tenacity of polypropylene yarn was determined by the procedure of ASTM test method D1577-64T with the filament denier determined with a Vibroscope. The denier of each filament in a cross section of yarn was first determined, and then the strength of each filament was determined with a Model TM Instron equipped with pneumatic clamps. The Instron was operated with an initial clamp separation distance of 1 inch and a separation rate of 2 in./min. The tenacity of each filament was determined by dividing the breaking strength by the denier and the average of these values for the filaments in a cross section of yarn was reported as the tenacity of the yarn.

c. Elongation at break

Elongation at break (as percentage of original specimen length) was determined from the stress-strain curve as recorded on the Instron chart.

d. Molecular orientation

The molecular orientation in a filament was determined by measuring the velocity of sound through the filament at a temperature of -18°C and calculating the orientation factor (α) according to the equation:

$$\alpha = 1 - C_1^2/C_2^2$$

where C_1 is the velocity of sound in the filament and C_2 is the velocity of sound in a polypropylene filament having no molecular orientation. The velocity of sound in unoriented polypropylene

filaments has been determined in previous work at the Institute to be 1.796 km/sec. Measurements of the velocity of sound in filaments were made with a KLH Pulse Propogation Meter.

e. Birefringence of filaments

The optical retardation of a filament was measured in a conventional manner with a polarizing microscope equipped with a quartz-wedge compensator. The diameter of the filament was measured with a microscope fitted with a calibrated micrometer eye piece. The birefringence was calculated by dividing the optical retardation by the diameter of the filament.

f. Refractive index

The refractive index of a filament was determined by the Becke immersion method with a polarizing microscope. In some cases, the refractive indices parallel to and perpendicular to the axis of the filaments were measured by the immersion method, and, in others, the refractive index was measured in only one direction by the immersion method and that in other the direction was calculated from the birefringence of the filament measured as described above.

g. Density

The density of a filament was measured by the gradient density tube method.

h. Crystallinity

The fraction crystalline (B) in filaments was calculated with the equation:[2]

$$B = 1.875 - \frac{1 - 0.983\rho}{(180 + t) - 4.8 \times 10^{-4}.\rho}$$

where ρ is the density of the filament and t is the temperature (°C) at which the density is measured.

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2. F. Dannusco, G. Moraglio, and G. Natta, Industrial des Plastrquies Modern, 10, 40 (1956).

2. Melt viscosity of polypropylene

Melt viscosity of polymers was measured with the equipment described in Section A-2 of the appendix. Approximately 4 g of a polymer was charged to the cylinder which was preheated to 233°C. With the orifice blocked, the piston was placed in cylinder and loaded with a weight of 2,200 g. After a 4-minute preheat period to melt the polymer, the orifice was opened to allow the polymer to flow. The rate of piston travel was recorded on the recording potentiometer. The time (in minutes) required for the piston to travel 1 inch was calculated and reported as the Extrusion Index.

3. Properties of fabrics

a. Breaking strength

The breaking strengths of both coated and uncoated fabrics were measured by the procedure described in Specification CCC-T-191, Method 5104.

b. Abrasion resistance

The abrasion resistances of fabrics were measured, with a Taber Abraser fitted with No. 18 Calibrade abrading wheels with 1000 g total load, in accordance with the method described in Specification CCC-T-191, Method 5306.

c. Blocking

The blocking tendency of a coated fabric at 105°C was evaluated by the procedure described in Specification CCC-T-191, Method 5872.

d. Coating adhesion

The strength of bond between a coating and a fabric was determined by applying the coating material to two pieces of fabric, placing these together with coating facing coating, curing the composite, and measuring the force required to separate the two pieces. The force required to separate the two pieces of fabric was measured with an Instron Model TM Tester following the procedure described in Specification CCC-T-191, Method 5970.